

Republic of Iraq
Ministry of Higher Education and Scientific Research
University of Anbar
College of Engineering
Dams And Water Resources Department

Third Class

Water Quality Control

By

Professor : Majeed M. Ramal

Lecture - 1

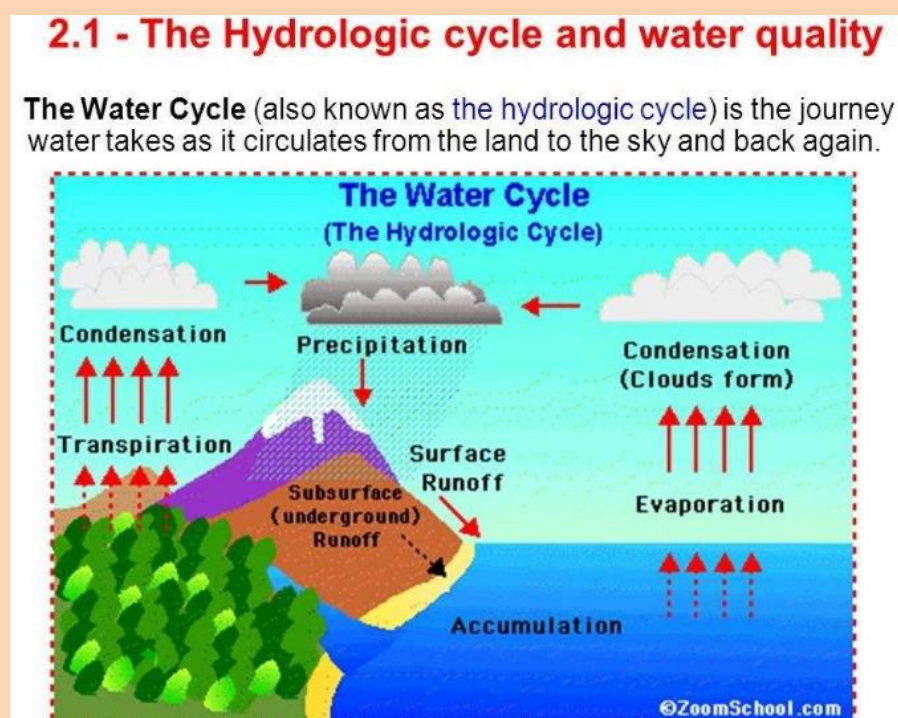
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 - Chemistry of solutions
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 - Alkalinity •Hardness,
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 - Metals
 - Organic
 - Nutrients , Nitrogen , phosphorus
- 4-Biological water –Quality parameter

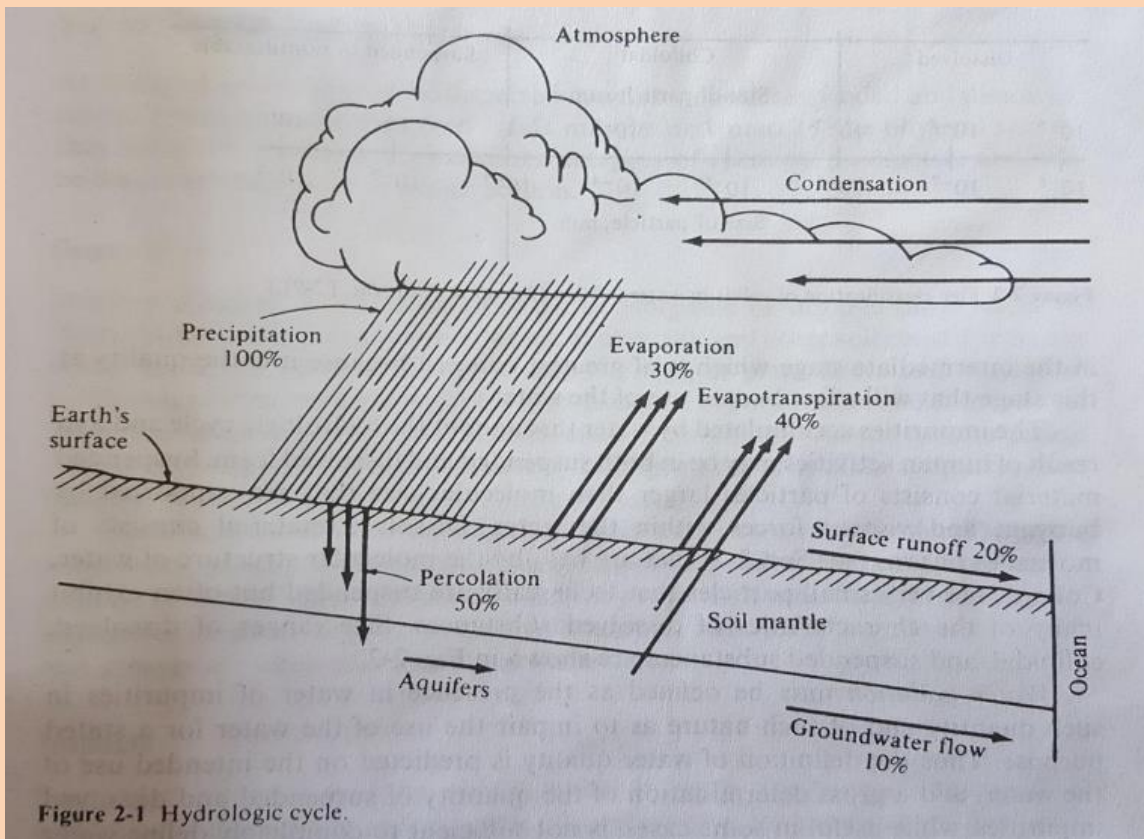
Water Quality

The availability of a water supply adequate in terms of both quantity and quality is essential to human existence. Early people recognized the importance of water from a quantity viewpoint. Civilization developed around water bodies that could support agriculture and transportation as well as provide drinking water. Recognition of the importance of water quality developed more slowly. Early humans could judge water quality only through the physical senses of sight, taste, and smell. Not until the biological, chemical, and medical sciences developed were methods available to measure water quality and to determine its effects on human health and well-being

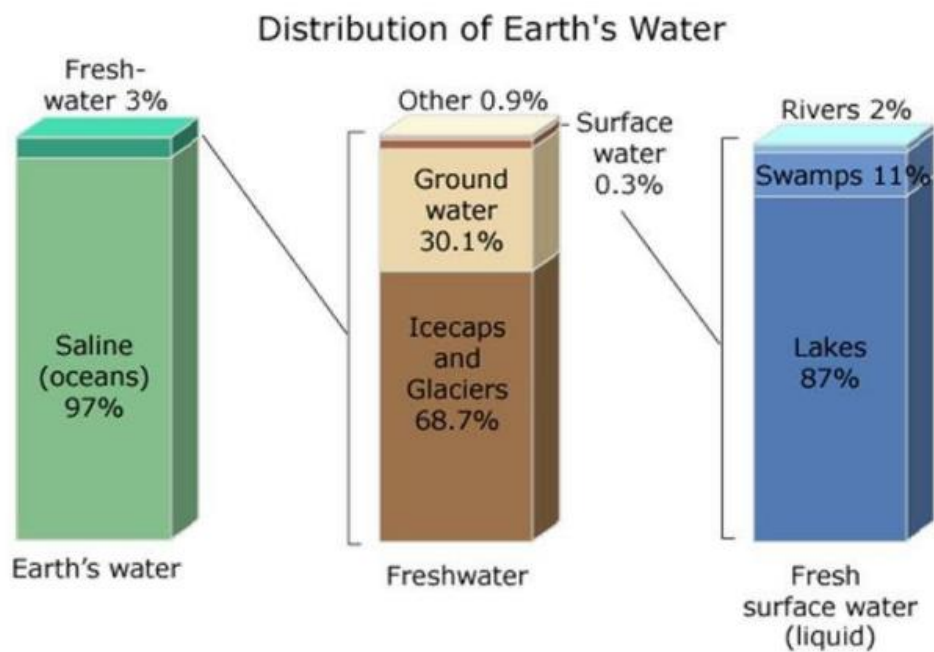
Like all sciences, the science of water quality has developed its own terminology and the means of quantifying these terms. The purpose of this lecture is to introduce the students and readers to the modern concepts of water quality. The means by which the nature and extent of contaminants in water are measured and expressed are presented along with the sources of various contaminants that find their way into water. An understanding of the material in this lecture will be essential in subsequent lectures dealing with water quality changes in both natural and engineered systems



WATER QUALITY CONTROL 3rd Stage



World Water Distribution



Size classification of solids in water

Type	Description	Size (mm)
Dissolved	Material consists of molecules or ions that are held by molecular structure of water.	$< 10^{-6}$
Colloidal	Very small particles that technically are suspended but often exhibit many of the characteristics of dissolved substances	$10^{-6} - 10^{-3}$
Suspended	Suspended material consists of particles that are supported by buoyant and viscous forces within water	$> 10^{-3}$

Physical water–quality parameters

- **Physical parameters** ... characteristics of water that respond to the senses of sight, touch, taste or smell.

2-2 Suspended Solids

- **Sources**
 1. **Inorganic** solids such as clay, silt, other soil constituents.
 2. **Organic** material such as plant fibers, biological solids (alge, bacteria)
 - natural contaminants from erosive action of flowing surface water,
 - domestic wastewater
 3. **Immiscible liquids** such as oils

- **Impacts**

1. It is displeasing and **provides adsorption sites** for chemical and biological agents.
2. May be **degraded biologically** resulting in objectionable by-products.
3. May **include disease causing organisms**

Measurement

- **Total Solid Test:**

- Quantifies **all the solids** in the water (suspended and dissolved),
- Measured by evaporating a sample at a temp. of 104°C to dryness and weighing the residue,
- Expressed as (mg/l) based on a dry mass of solids per volume,

- **Suspended Solid Test**

fraction of the solids in water sample can be approximated by filtering the water, and drying the residue at 104°C and determining the mass of the residue retained on the filter.

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- The amount of **dissolved solids** passing through the filters, is the **difference** between the **total-solids** and the **suspended solids** of a water sample.
- **Note:**
 - Some colloids may pass through the filter and then it is measured with the dissolved fraction while some of the dissolved solids adsorb to the filter material.
 - It depends on the size and nature of solids and on the pore size and surface characteristics of the filter material.
- The total **organic content** of both total and suspended solids can be determined by firing the residues at 600 °C for 1hr. The organic material will be converted to carbon dioxide, water and vapor. The remaining material will represent the inorganic residue
- **Use:**
 - Suspended Solid is an important parameter of wastewater in measuring the quality of the wastewater influent and monitor several treatment processes.
- **EPA** set a max. SS of **30 mg/l** for most treated wastewater discharge.

Example 2.1

- The tare mass of the pair = 54.352 g
- Volume of sample = 250 ml drawn through a filter pad, then placed in a drying oven at 104 °C, a constant mass of 54.389 g is reached.
- **Determine** the suspended solids concentration of the sample.

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Solution

- Determine the mass of solids removed.
-
- Tare mass + solids = 54.389 g
- Tare mass = 54.352g
-
-
- Mass of solids = 0.037g
- = 37 mg
- Determine the concentration of the solids
- mg solids x 1000 mL /L
- _____ = conc. in mg /L
- mL of sample
-
- 37x 1000
- _____ = 148 mg /L
- 250

- Example :
- 100 mL of water
- Dry filter = 0.254 gm
- After 104 c = 0.263 gm
- After 600 c = 0.258 gm
- Sol.
- $S.S = 0.263 - 0.254 / 0.1 \text{ L} = 0.09 \text{ g/L} = 90 \text{ mg/L}$
- $V.S.S = 0.263 - 0.258 / 0.1 = 0.05 \text{ g/L} = 50 \text{ ppm}$
- $F.S.S = 40 \text{ mg/L}$

2.3 Turbidity

- **What is Turbidity?**

A measure of the extent to which light is either absorbed or scattered by suspended material in water.

- Turbidity is not a quantitative measurement of suspended solids ... why? (small pebble of glass)
- Test of turbidity is commonly for **natural bodies** of water or **potable (drinking) water** where the nature and effects of the solids are more important than quantity.

Source

- Erosion of colloidal material such as clay, silt, rock fragments, oxides from the soil.
- Vegetable fibers and microorganisms,
- Soap, detergents.

Impacts

- Turbid water is **displeasing**
- Provide adsorption sites for **chemicals** that may be **harmful** or cause undesirable taste and odor.
- the presence of tiny colloidal particles makes it more difficult to remove,
- **Disinfection** of turbid water is difficult (adsorption)
- Accumulation of turbidity causing particles in streambeds result in **sediment depositions**... surface water bodeis

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Measurement

- Generally, turbidity is measured by determining the percentage of light of a given intensity that is either absorbed or scattered.
- Jackson turbid-meter.
- Turbidity is measured using a **turbidity meter**.
- Formazin, a chemical compound, is currently used as the primary standard for calibrating turbid meters,
- Turbidity meter readings are expressed as a formazin turbidity units (**FTU**) and the results are reported as nephelometric turbidity units (**NTU**).

Use

- Natural waters have turbidity ranging from few FTUs to several hundred.
- **EPA** ... maximum **1 FTU** for drinking water.

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Lecture - 2

2.4 Color

- Pure water is colorless.
- Foreign substances in water cause color.
- **Apparent color** : due to suspended matter,
- **True color**: due to dissolved solids after removal of suspended matter.

Source

- Industrial wastes, food processing, chemical production...etc
- Reddish water Iron oxides
- Yellowish-brownorganic debris, leaves, wood
- Brown or blackish water Manganese oxides

Impacts

- Not acceptable to the public
- Unsuitable in industrial use
- Reduce the effectiveness of disinfection process
- (some organic compounds with chlorine result in cancer-causing agents)

Measurement

- Color can be measured visually by comparison with potassium chloroplatinate standards True color unit (TCU),
- or by scanning at different spectro-photo-metric wavelengths.

Use

- Color is an indirect measurement of foreign substances in water.

Impacts

- Not acceptable to the public
- Unsuitable in industrial use
- Reduce the effectiveness of disinfection process
- (some organic compounds with chlorine result in cancer-causing agents)

Measurement

- Color can be measured visually by comparison with potassium chloroplatinate standards True color unit (TCU),
- or by scanning at different spectro-photo-metric wavelengths.

Use

- Color is an indirect measurement of foreign substances in water.

2.5 Taste and Odor

Source

- Inorganic substances produce tastes; alkaline materialbitter taste, metallic material Salty or bitter taste.
- Organic material produce both taste and odor
- Biological decomposition of organics result in taste and odor.

Impacts

- displeasing (water is odorless and tasteless), associated with contaminants
- Some organic substances which cause odor may be carcinogenic.

Measurement

Threshold odor number (TON)

- Odor-free water (B) is used for successive dilutions of the sample with odor free water (A) until the odor is no longer detectable to make 200 ml mixture.

$$\text{TON} = (A+B)/A$$

Where: A is the volume of odorous water (mL)

B is the volume of odor-free water (mL)

Use

- Taste and odor are associated with potable water and wastewater.
- EPA ... max. of 3 TON

- Example
- $A = 100 \text{ mL}$
- $B = 550 \text{ mL}$
- $\text{TON} = A + B/A$
- $\text{TON} = 100 + 550 / 100 = 6.5$

2.6 Temperature

One of the most important parameter in natural surface water systems;

- Related to presence and activities of biological species,
- Affect chemical reactions
- Affect solubility of gases in water

Impacts

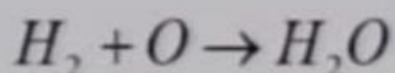
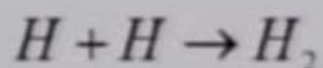
- Increasing temperature ... increase biological activities ... may cause problems,
- Affect physical properties of water (viscosity, density)

Chemical water – quality parameters

- Water is called a **universal Solvent**
- Chemical parameters of water are:
 1. Total dissolved solids,
 2. Alkalinity,
 3. Hardness,
 4. Fluorides,
 5. Metals,
 6. Organics,
 7. Nutrients.

Chemistry of solutions

- **Atom** the smallest unit of element
- **Molecules** of elements or compounds are constructed of atoms.



- **Molecular mass** is the sum of the atomic mass of all atoms in molecule

For example :

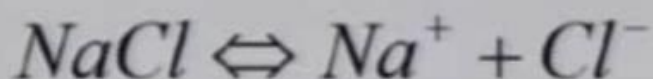
- Atomic mass of oxygen (O) = 16 , for Hydrogen (H) =1
- Molecular mass for water (H₂O) =18

- **A mole** of an element or compound is its molecular mass in gm.

For example :

one mole of oxygen (O₂) = 32, water (H₂O) =18

- One mole of a substance dissolved in sufficient water to make one liter of solution is called a **one molar solution**.
- The charged species is called **ions**. Produced when compounds dissociate in water.
- +ve ions called **cations**, -ve ions called **anions**
- **Neutrality** means the number of cations = the number of anions.



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- **The valence** is the number of charges on an ion.
The valence of $(\text{Na}^+)=1$,
The valence of $(\text{Cl}^-)=1$
- **The equivalence** of an element is the number of hydrogen atoms that element can hold in combination or can replace in a reaction (= valence in most cases)
- **An equivalent** of an element is its gram molecular mass (mole) divided by its equivalence.
- **A milliequivalent** of an element is its milligrams molecular mass divided by its equivalence.

Example

How many grams of calcium will be required to combine with 90 g of carbonate to form calcium carbonate?

Solution:

1- One equivalent of Carbonate $(\text{CO}_3^{2-}) = \frac{\text{equivalent mass}}{\text{equivalence}} = \frac{12 + 3(16)}{2} = 30 \text{ g / equiv}$

2- One equivalent of Calcium $(\text{Ca}^{2+}) = \frac{40}{2} = 20 \text{ g / equiv}$

3- The no. of equivalents of Carbonate must equal to the no. of equivalents of calcium.

4- No. of equivalents of calcium $= \frac{90 \text{ g}}{30 \text{ g / equiv}} = 3 \text{ equiv}$

5- So, we need 3 equiv of carbonate $= 3 \text{ equiv} \times 20 \text{ g / equiv} = 60 \text{ g.}$

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- The concentration of substance **A** can be expressed as an equivalent concentration to substance **B** as the following:

$$\frac{(g/L)A}{(g/equiv)A} \times (g/equiv)B = (g/L)A \text{ expressed as } B$$

- Generally, the constituents of dissolved solids are reported in terms of equivalent calcium carbonate concentrations

Example

What is the equivalent calcium carbonate concentration of:

- 117 mg/L of NaCl?
- 2×10^{-3} mol/L of NaCl?

1- One equivalent of Calcium Carbonate (CaCO_3)

$$= \frac{\text{equivalent mass}}{\text{equivalence}} = \frac{40 + 12 + 3(16)}{2} = 50 \text{ g/equiv}$$

2- One equivalent of Sodium Chloride (NaCl) = $\frac{23 + 35.5}{1} = 58.5 \text{ g/equiv}$

$$\frac{117(\text{mg/L})\text{NaCl}}{58.5(\text{g/equiv})A} \times 50(\text{g/equiv})\text{CaCO}_3 = 100(\text{mg/L})\text{NaCl as CaCO}_3$$

3- One mole of a substance divided by its valence is one equivalent →

$$\frac{2 \times 10^{-3} \text{ mol/L}}{1 \text{ mol/equiv}} = 2 \times 10^{-3} \text{ equiv/L}$$

$$\text{thus, } 2 \times 10^{-3} \text{ equiv/L} \times 50(\text{g/equiv})\text{CaCO}_3 = 100(\text{mg/L})\text{NaCl as CaCO}_3$$

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Lecture - 3

Total Dissolved solids

The material remaining in the water after filtration for the suspended solid analysis is considered to be **dissolved solids**.

- **Source**

- Results from the solvent action of water on solids, liquids, and gases.
- Inorganic dissolved solids; minerals, metals, gases.
- Organic ; decay products of vegetation, organic chemicals and gases.

Impacts

- Produce tastes, colors, and odor,
- Some chemicals are toxic or carcinogenic,
- Some dissolved solids may combine to form a compound of more dangerous than the original materials,
- Not all dissolved solids are undesirable.

Measurement

- See sec. 2-2 Suspended Solids
- By measuring the electrical conductivity of the water, Conductivity measures the ability of water to conduct an electrical current.

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- Conductivity is a good way to determine the ionic strength of water because the ability of water to conduct a current is proportional to the number of ions in the water
- Freshwater generally has low conductivity measured in microSiemens (μS)
- Marine systems have much higher conductivity measured in milliSiemens (mS) which can easily be converted to salinity
- Humans and other terrestrial animals require fresh water for survival as do plants and animals normally found in freshwater

Use

- TDS parameter is important in the analysis of water and wastewater to know more about the composition of the solids in water

ION BALANCE:

It is possible to check whether this is true by performing an Ionic Balance calculation. This check should return a value of 0% if cations and anions are perfectly in balance, although it is accepted that values between $\pm 10\%$ are satisfactory for this test. When values are outside the $\pm 10\%$ range, there is often an assumption that some part of the analysis is wrong. However, often there are other explanations.

The Ionic Balance Calculation should encompass all anions and all cations with the sample. However, commercially this is not viable and a range of different calculations are available that cover the most commonly encountered cations and anions, such as the examples below

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Common Cations	Common Anions
Calcium Ca ²⁺	Chloride Cl ⁻
Magnesium Mg ²⁺	Sulphate SO ₄ ²⁻
Sodium Na ⁺	Alkalinity HCO ₃ ⁻
Potassium K ⁺	Phosphate PO ₄ ³⁻
Iron Fe ²⁺	Nitrate NO ₃ ⁻
Ammoniacal Nitrogen NH ₄ ⁺	
Manganese Mn ²⁺	
Aluminium Al ³⁺	

Secondary Anions :Iron , Sr, CO₃⁻² , F⁻¹ , Si...

Ideally, therefore, we can state :anions (meq/L) = cations (meq/L)

To convert from mg/L to meq /L, the following formula is used

Meq/ L = mg/L (Charge/ Atomic Mass) = mg/L(Equivalent Weight)

To carry out this conversion we need to know the relationship between the mass and the charge for each species. Some examples are shown in the following table

Ion	Charge	Mass	Equivalent Wt	Multiply by (to convert g.m to meq/L)
H ⁺	1	1	1.0	1.0
Na ⁺	1	23.0	23.0	0.0435
K ⁺	1	39.1	39.1	0.0256
Ca ²⁺	2	40.1	20.05	0.0499
Mg ²⁺	2	24.3	12.15	0.0823
Fe ²⁺	2	55.9	28.0	0.0357
Zn ²⁺	2	65.4	32.7	0.0306
NH ₄ ⁺ (as N)	1	14.0	14.0	0.0714
HCO ₃ ⁻	1	61.0	61.0	0.0164
CO ₃ ²⁻	2	60.0	30.0	0.0333
Cl ⁻	1	35.5	35.5	0.0282
F ⁻	1	19.0	19.0	0.0526
SO ₄ ²⁻	2	96	48.0	0.0208
NO ₃ ⁻ (as N)	1	14.0	14.0	0.0714
H ₂ PO ₄	1	97	97	0.0103

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Ion Balance

The dissolved solids content of natural water is classified to:

- **Major constituents** ... (1-1000mg/L)

sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-)

- Called **common ions**,
 - Measured individually and summed on an equivalent basis to represent the approximate **TDS**,
 - The sum of anions must equal the sum of cations (**as a check**)
- **Secondary constituents** (0.01-10mg/L).
Iron, potassium, carbonate, nitrate, fluoride, boron, silica

Testing for ion balance

- The results of common ions for a sample of water are shown below,
- If 10% error in the balance is acceptable, should the analysis be considered complete?

sodium (Na^+) = 98mg/L,

calcium (Ca^{2+}) = 55mg/L,

magnesium (Mg^{2+}) = 18mg/L,

bicarbonate (HCO_3^-) = 250mg/L,

sulfate (SO_4^{2-}) = 60mg/L,

chloride (Cl^-) = 89 mg/L

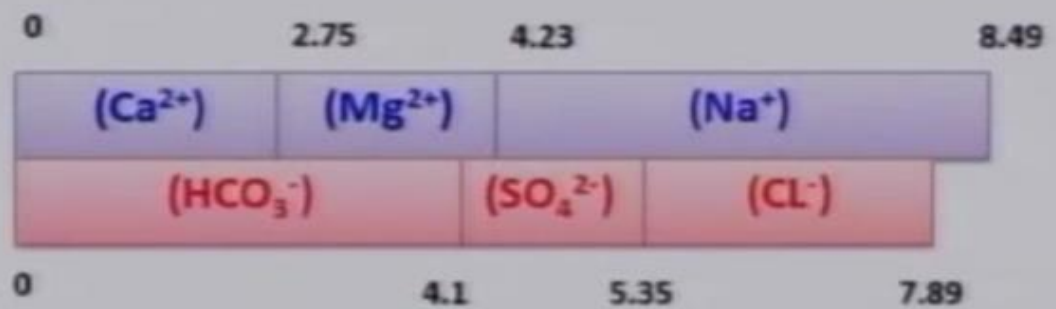
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Ion	Concentration (mg/L)	Equiv, (mg/mequiv)	Equiv conc, (mequiv/L)
(Na ⁺)	98	23/1	4.26
(Ca ²⁺)	55	40/2	2.75
(Mg ²⁺)	18	24.3/2	1.48
			8.49
(HCO ₃ ⁻)	250	61/1	4.1
(SO ₄ ²⁻)	60	96/2	1.25
(CL ⁻)	89	35.5/1	2.51
			7.86

- Calculate the percent of error

$$e\% = ((8.49 - 7.89) / 7.89) * 100\% = 8\% < 10\% \dots \text{Accept analysis}$$



Bar diagram

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$$\text{Ca}(\text{HCO}_3)_2 = 2.75 \text{ meq /L}$$

$$\text{Mg}(\text{HCO}_3)_2 = (4.1 - 2.75) = 1.35 \text{ meq/L}$$

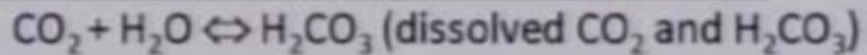
$$\text{MgSO}_4 = (4.23 - 4.1) = 0.22 \text{ meq/L}$$

$$\text{Na}_2\text{SO}_4 = (4.35 - 4.23) = 0.12 \text{ meq/L}$$

$$\text{NaCl} = (4.35 - 4.23) = 2.51 \text{ meq/L}$$

- CO_2 influences the carbonate system in water as follows:

Carbon dioxide dissolves in water and produces carbonic acid

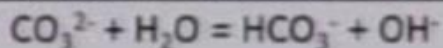


Carbonic acid dissociates producing H^+

1. $\text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^-$ (HCO_3^- can absorb another H^+ to become H_2CO_3)
2. $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$ (CO_3^{2-} can absorb one H^+ to become HCO_3^-)

- The ability of water to absorb H^+ ions (anions) without a change in pH is known as its **alkalinity**.
- In freshwater, alkalinity typically is due to the presence of excess carbonate anion (from the weathering of silicate or carbonate rocks) that when hydrolyzed produces OH^- (and neutralizes H^+) as follows:

Hydrolysis of carbonate and carbonate produces OH^-



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Lecture – 4

Alkalinity

Alkalinity Definition :

is defined as the quantity of ions in water that will react to neutralize hydrogen ions . alkalinity is thus a measure of the ability of water to neutralize acids.

*Without this acid-neutralizing capacity, any acid added to a stream would cause an immediate change in the pH.

Algae remove $\text{CO}_2 \rightarrow \text{pH } 9-10$

The Standard Limit of drinking water range (6.5 – 8.5)

Increasing Alkalinity leads to Low Hydrogen Ion Concentration then High pH value .

Sources:

Constituents of Alkalinity in natural water system include:

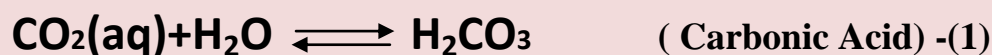
(CO_3^{-2} , HCO_3^{-1} , OH^{-1} , HSiO_3^{-1} , $\text{H}_2\text{BO}_3^{-1}$, HPO_4^{-2} , HS^{-1} and NH_3^0)

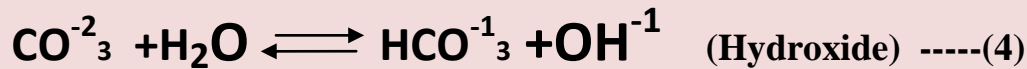
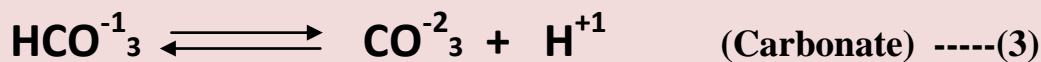
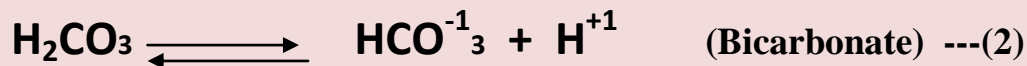
These Compounds result from,dissolution of mineral substances and basic materials in the soil and atmosphere Phosphate (HPO_4^{-2}) also may originate from detergents in wastewater discharges and from fertilizers and insecticides from agricultural land.

Hydrogen sulfide and Amonia may be products of microbial decomposition of organic material.

The most common Constituents of Alkalinity. Are (CO_3^{-2} , HCO_3^{-1} , OH^{-1}).

In addition to their mineral origin , these substances can originate from Carbon Dioxide (CO_2) , a Constituent of the atmosphere and product of microbial decomposition of organic material. These reactions are as follow :





The reaction represented by the equation No. (4) is a weak reaction chemically.

However , utilization of the Bicarbonate ion as carbon source by algae can drive the reaction to the right and result in substantial accumulation of OH^{-1} . Water with heavy algal growth often has pH values as high as 9 to 10 .

Impacts :

In large quantities , Alkalinity imparts a Bitter Taste to Water , the principal objectionable of alkaline water , is the reactions that occur between alkalinity and certain Cations in the water to Produce precipitates (Solids) can foul pipes and other water system appurtenance .

Measurement :

Alkalinity measurement are made by titrating the water with an acid and determining the hydrogen equivalent.

Titration: A titration is a technique where a solution of known concentration is used to determine the concentration of an unknown solution. Typically, the titrant (the know solution) is added from a [buret](#) to a known quantity of the analyte (the unknown solution) until the reaction is complete. Knowing the volume of titrant added allows the determination of the concentration of the unknown. Often, an indicator is used to usually signal the end of the reaction, the endpoint.

Alkalinity is then expressed as milligrams per liter as CaCO_3 .

If 0.02 NH_2SO_4 is used in the titration , then (1 ml) of the acid will neutralize (1mg) of alkalinity as CaCO_3 .

Hydrogen ions from the acid react with the alkalinity according to the following equations :

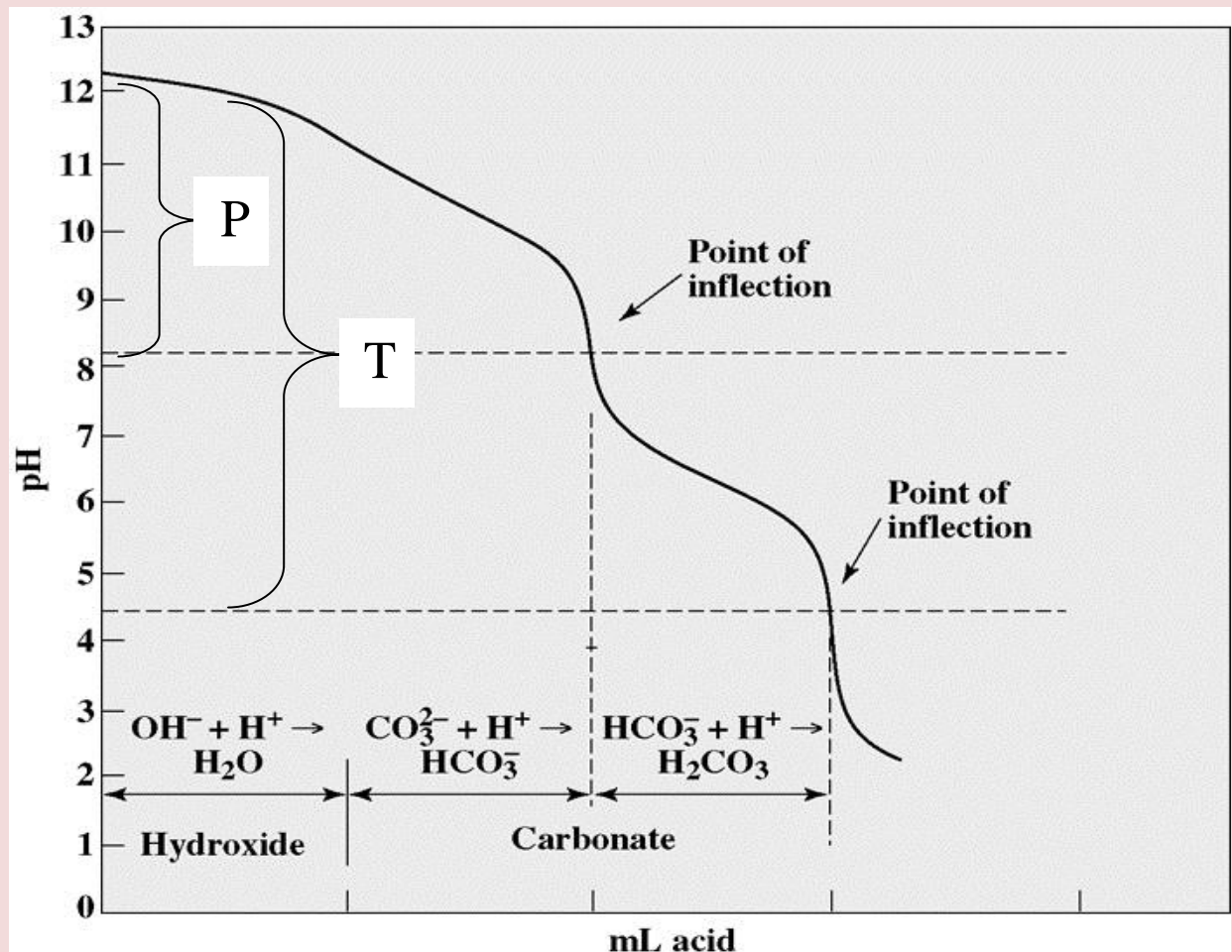
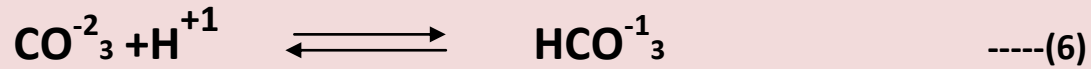
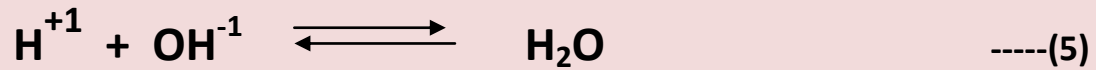


Figure -4 :Alklinity Titration Curve

If acid is added slowly to water and the pH is recorded for each addition . a titration curve similar to the curve in Fig1 above is obtained .Of particular significance are the inflection points in the curve that occur at approximately pH (8.3) and ((4.5) . The conversion of carbonate to bicarbonate (Eq'n 6) is essentially complete at (pH = 8.3) .However, because bicarbonate is also alkalinity species , an equal amount of acid must be added to complete the neutralization . Thus , the neutralization of carbonate is only one –half complete at (pH = 8.3), all of the hydroxide and one –half of the carbonate have been measured at (pH=8.3)

We use phenolphthalein Indicator (Pink), to know the first inflection point when end point-pink to colorless

. At pH=4.5 all of the bicarbonate has been converted to carbonic acid (Eq'n 7) , Including the bicarbonate resulting from the reaction of the acid and carbonate (Eq'n 6).

We use mixed-bromo cresol green methyl Indicator (Green), to know the second inflection point when end point-Green to Red.

Thus, the amount of acid required to titrate a sample to pH=4.5 is equivalent to the total alkalinity of the water

. This point is illustrated in the following examples .

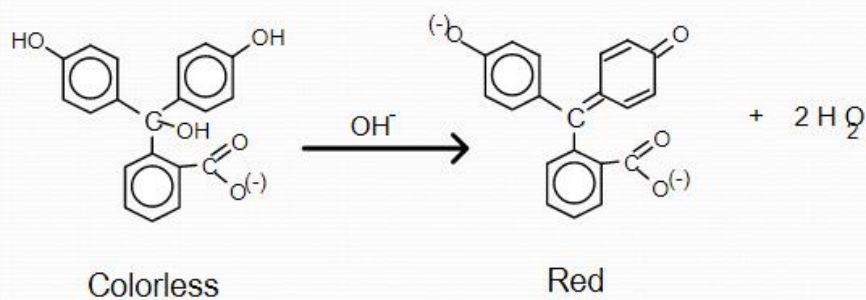
Alkalinity is calculated using the following Eq'n :

$$\text{Alkalinity} \left(\frac{\text{mg}}{\text{L}} \text{ as } \text{Ca CO}_3 \right) = \frac{\text{mL (Titrant)} \times \text{Normality of Acid} \times 50000}{\text{mL of Sample}} \text{--Eq'n (8)}$$

Phenolphthalein

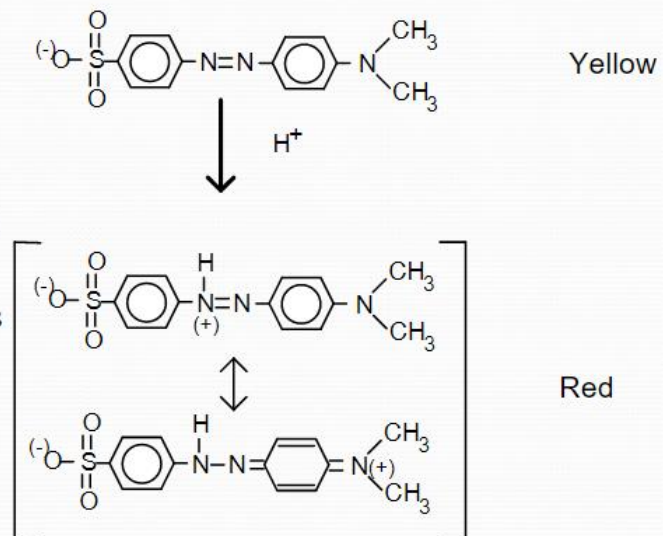
- used as a colorimetric indicator of alkalinity and acidity first endpoint
 - changes color at about pH 8.3
 - pH signifies loss of OH^- and where all carbonates are as HCO_3^-

Pink to colorless



Methyl Orange

- used as a colorimetric indicator of the final alkalinity titration endpoint
 - changes color at about pH 4.5
 - where all carbonates are as H_2CO_3



Example-1 : (Determining total alkalinity)

A 200-mL sample of water has an initial pH of 10. Thirty milliliter of 0.02NH₂SO₄ is required to titrate the sample to pH = 4.5 . What is the total alkalinity of the water in milligram per liter as CaCO₃ ?

SOLUTION:

Using Eq'n No. (8)

$$\text{Alkalinity} \left(\frac{\text{mg}}{\text{L}} \text{ as Ca CO}_3 \right) = \frac{\text{mL} (30) \times 0.02 \times 50000}{200 \text{ mL}} = 150 \frac{\text{mg}}{\text{L}} \text{ as Ca CO}_3$$

Example-2 : (Determining total alkalinity)

A 100-mL sample of water is titrated for alkalinity determining. (3.0) milliliter of 0.02NH₂SO₄ is required to reach the phenolphthalein end point-pink to colorless, and an additional (12) mL is added for the mixed bromo cresol green methyl color change . Calculate the phenolphthalein alkalinity, the mixed-bromo cresol green methyl alkalinity and the total alkalinity ?

. What is the total alkalinity of the water in milligram per liter as CaCO₃ ?

SOLUTION:

Using Eq'n No. (8)

$$1 - \text{Phenolphthalen Alkalinity} \left(\frac{\text{mg}}{\text{L}} \text{ as Ca CO}_3 \right) = \frac{\text{mL} (3) \times 0.02 \times 50000}{100 \text{ mL}} = 30 \frac{\text{mg}}{\text{L}} \text{ as Ca CO}_3$$

$$2 - \text{mixed} - \text{bromo cresol green methyl Alkalinity} \left(\frac{\text{mg}}{\text{L}} \text{ as Ca CO}_3 \right) = \frac{\text{mL} (12) \times 0.02 \times 50000}{100 \text{ mL}} = 120 \frac{\text{mg}}{\text{L}} \text{ as Ca CO}_3$$

$$3 - \text{Total Alkalinity} \left(\frac{\text{mg}}{\text{L}} \text{ as Ca CO}_3 \right) = \frac{\text{mL} (15) \times 0.02 \times 50000}{100 \text{ mL}} = 150 \frac{\text{mg}}{\text{L}} \text{ as Ca CO}_3$$

$$\begin{aligned} \text{Or Total Alk.} &= \text{Phenolphthalen Alk.} + \text{Mixed- bromo cresol Alk} = \\ &= 30 + 120 = 150 \frac{\text{mg}}{\text{L}} \text{ as Ca CO}_3 \end{aligned}$$

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Water Quality Control

By

Assistant Professor : Majeed M. Ramal

Lecture – 5

Alkalinity

Alkalinity Species :

If the volume needed to reach the (8.3) end point is known , the species of alkalinity can also be determined . Because all of the hydroxide and one-half of the carbonate have been neutralized at pH 8.3 , the acid required to lower the pH from 8.3 to 4.5 must measure the other one-half of the carbonate , plus all of the original bicarbonate. If (P) is the Alkalinity to reach pH 8.3 and (T) is the total quantity of Alkalinity required to reach pH 4.5 , the following generalization concerning the forms of alkalinity can be made :

- Hydroxide and bicarbonate alkalinities cannot be present at the same time (incorrect but rough estimate), @pH8.3 neutralization of hydroxides are completed.

Five possible situations:

1. If $P = T$, all alkalinity is Hydroxide only , initial pH = 10

Hydroxide (OH^-) alkalinity is present if phenolphthalein alkalinity is more than half the total alkalinity.

$$\text{OH}^- \text{ Alk.} = \text{Caustic Alk.} = \text{Total Alkalinity} = T$$

2. If $P = T/2$, all alkalinity is Carbonate only , initial pH = 9.5

Carbonate (CO_3^{2-}) alkalinity is present when phenolphthalein alkalinity is not zero but is less than total alkalinity.

$$(\text{CO}_3^{2-}) \text{ alkalinity} = 2 \times \text{Caustic Alk.} = 2P = \text{Total Alkalinity}$$

3. If $P = 0$ all alkalinity is Bicarbonate only , initial , (pH ≤ 8.3)

Bicarbonate (HCO_3^-) alkalinity is present if phenolphthalein alkalinity is less than half the total alkalinity.

$$(\text{HCO}_3^-) \text{ alkalinity} = T = \text{Total Alkalinity}$$

4. If $P < T/2$, alkalinity are CO_3^{2-} and HCO_3^- . ($8.3 > \text{pH} < 10.5$)

$$(\text{CO}_3^{2-}) \text{ alkalinity} = 2 \times \text{Caustic Alk.} = 2P$$

$$(\text{HCO}_3^-) \text{ alkalinity} = T - 2P = \text{Total Alkalinity} - (\text{CO}_3^{2-}) \text{ alkalinity}$$

5. If $P > T/2$, alkalinity are OH^- and CO_3^{2-} , initial pH = 10

$$(\text{OH}^-) \text{ alkalinity} = 2P - T, \quad (\text{CO}_3^{2-}) \text{ alkalinity} = 2(T - P)$$

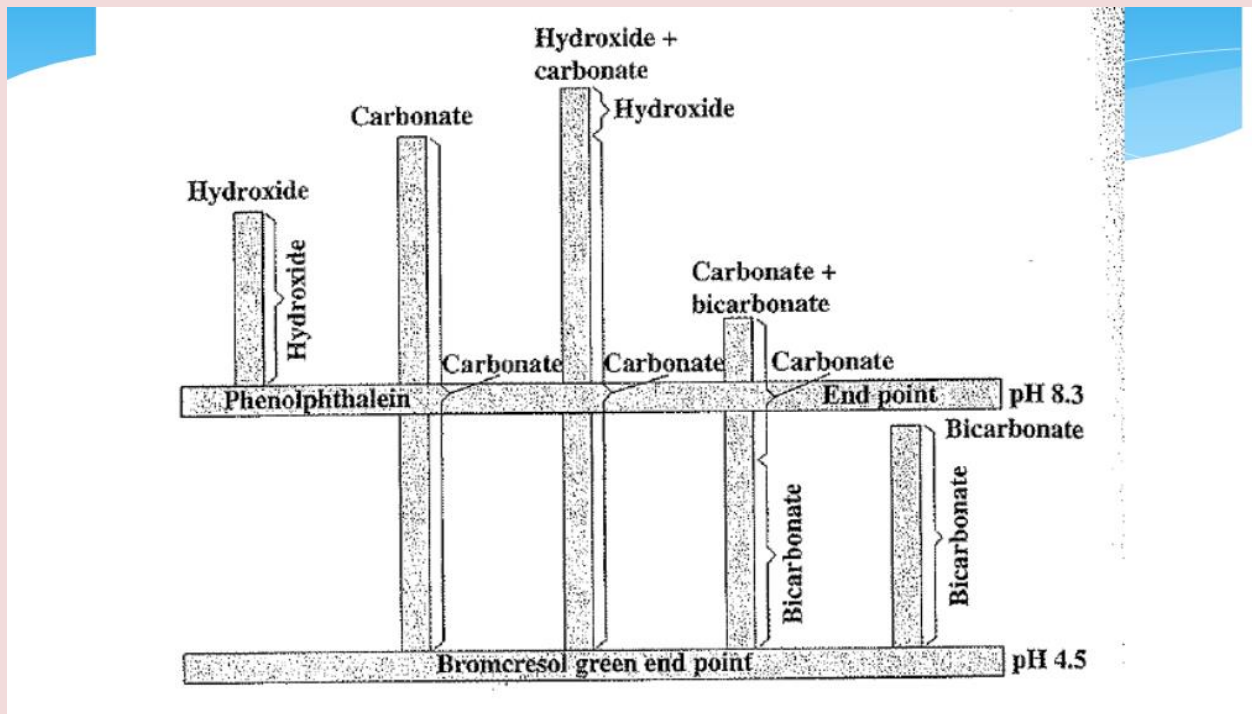


Figure -2 Graphical representation of titration of samples containing various forms of alkalinity

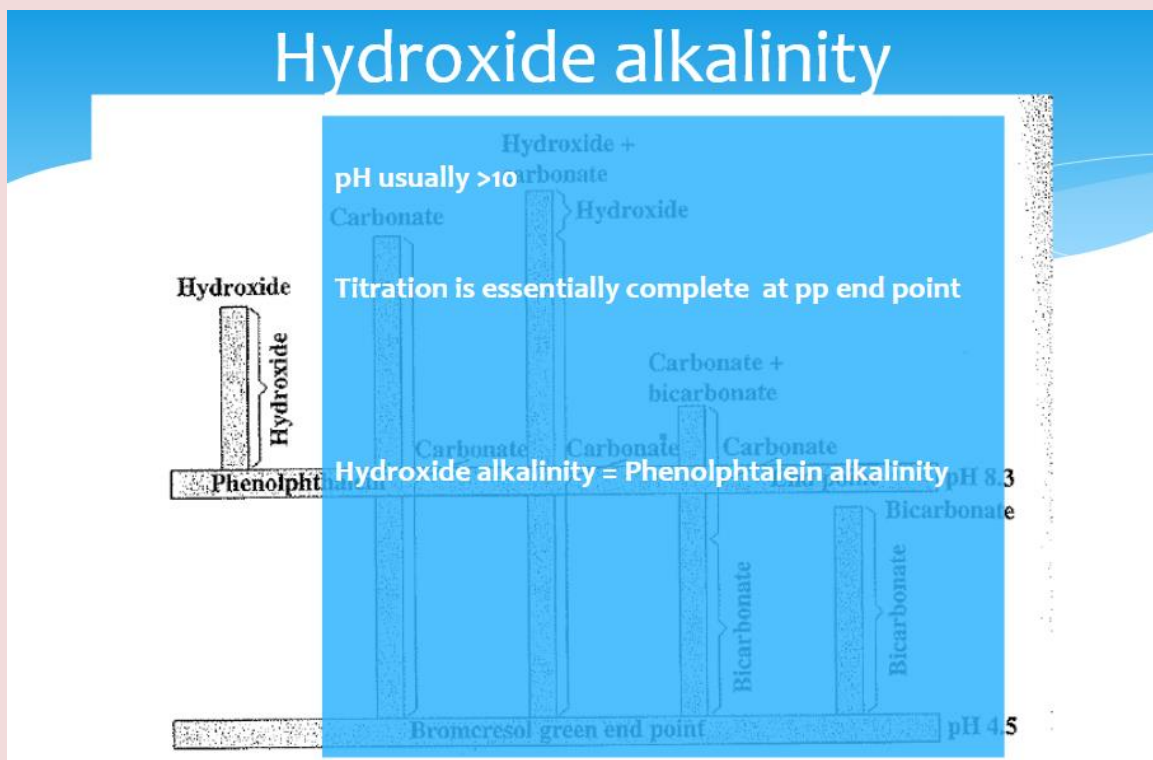


Figure -3 Graphical representation of titration of samples containing Hydroxide of alkalinity

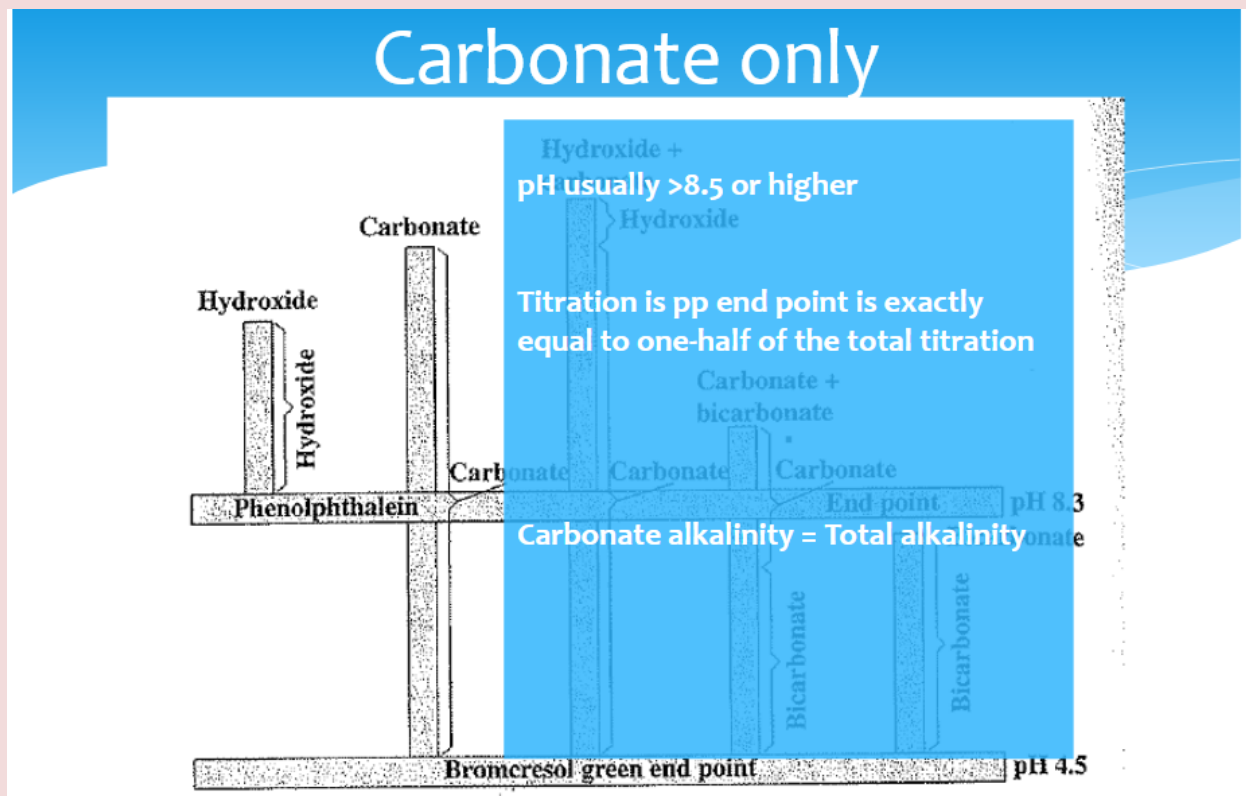
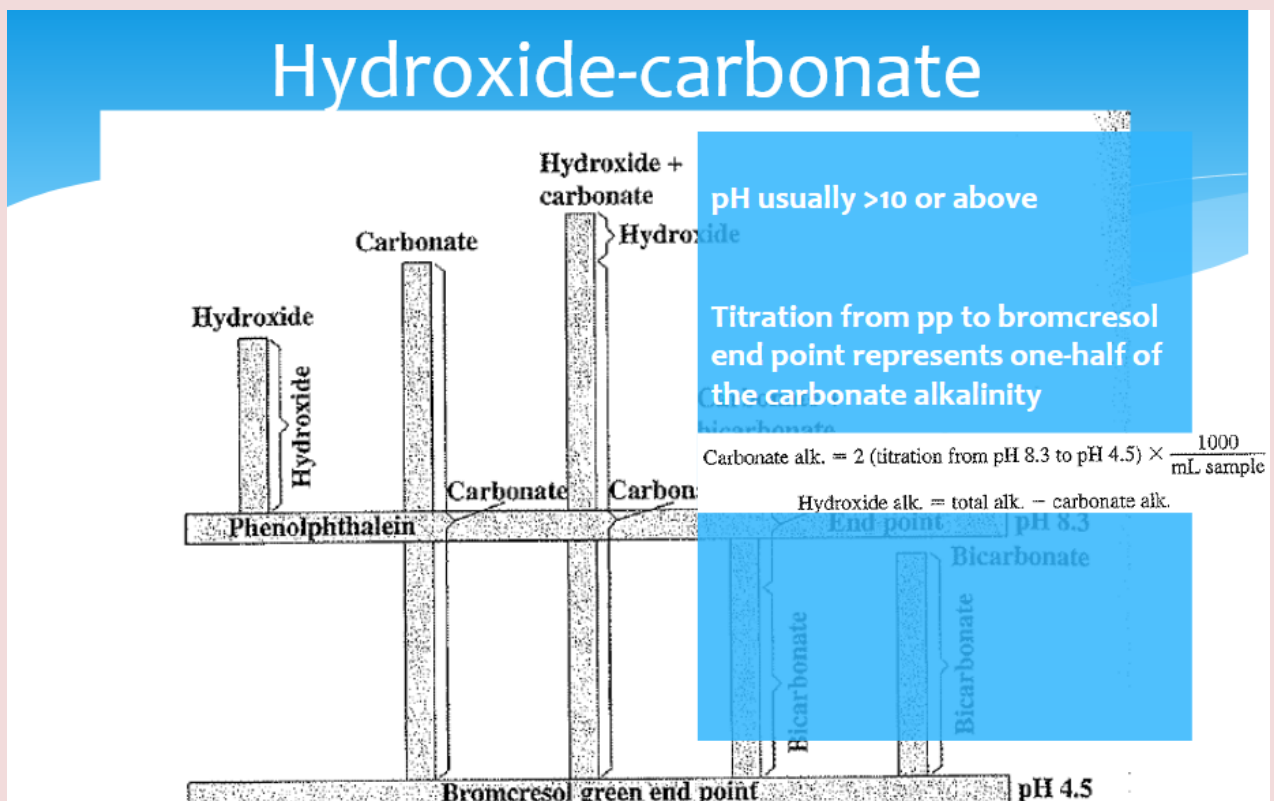


Figure -4 Graphical representation of titration of samples containing Carbonate of alkalinity



Carbonate-bicarbonate

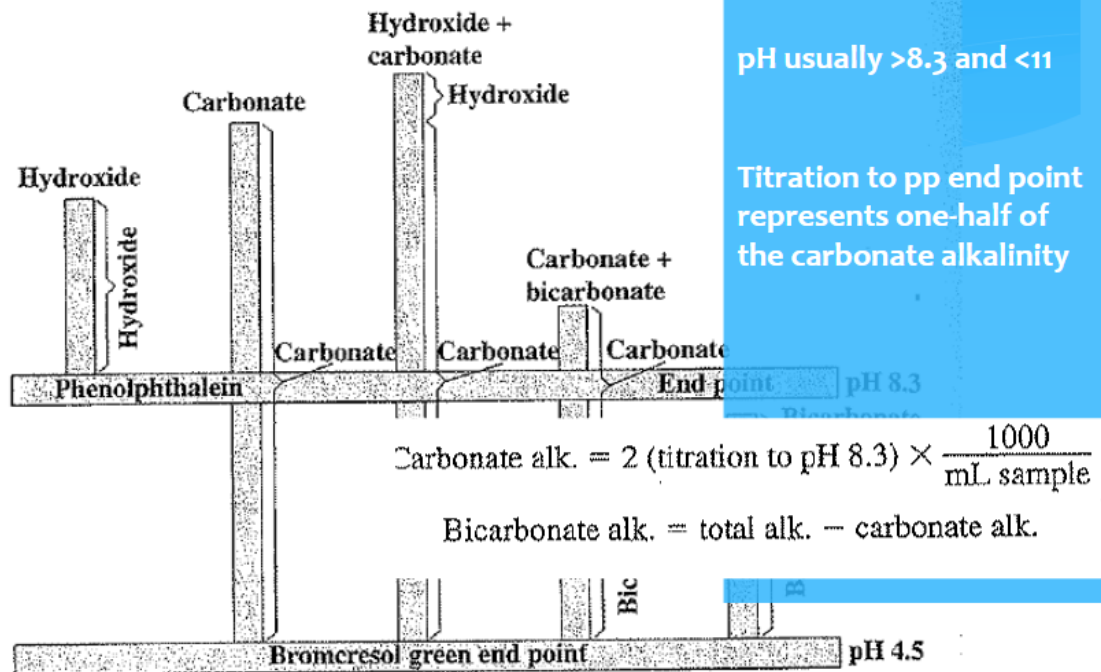


Figure -6 Graphical representation of titration of samples containing Carbonate - Bicarbonate of alkalinity

Bicarbonate

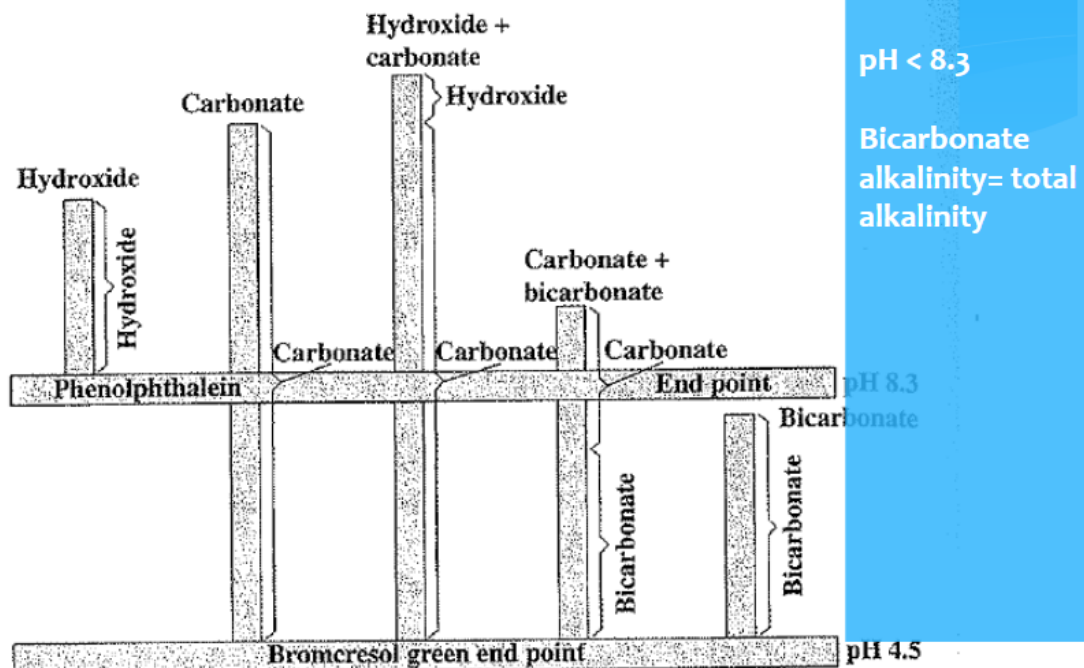


Figure -7 Graphical representation of titration of samples containing Bicarbonate of alkalinity

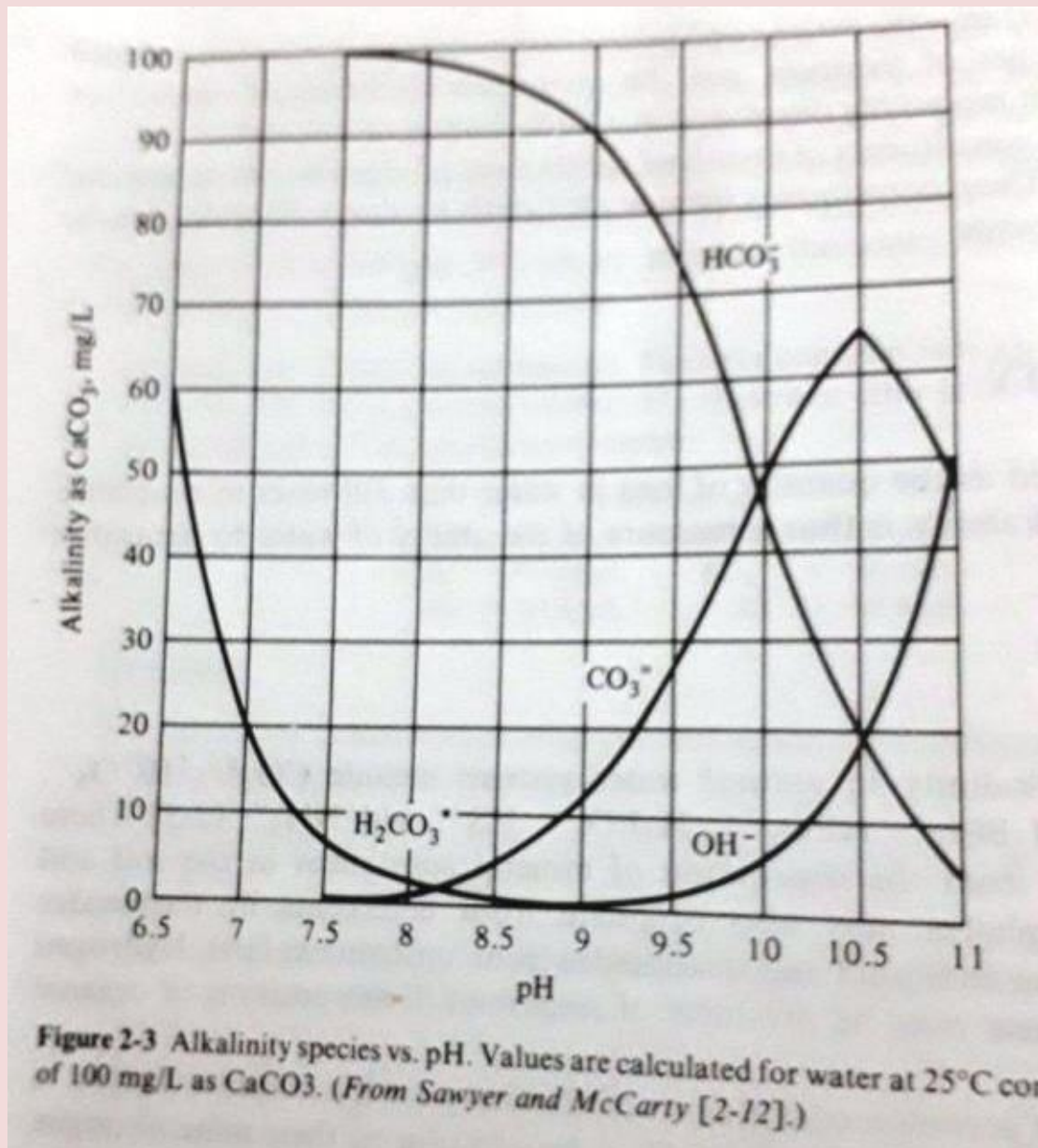


Figure -8 Alkalinity species vs. pH values

Example -3:

In alkalinity determination using (0.02 N Acid), (1 mL = 1 mg calcium carbonate).
A 100 mL sample of water gave the following results:-

Titration to pH = 8.3 (Phenolphthalein change color) added 14.5 mL Acid.

Total titration to pH = 4.5 (mixed bromo cresol change color) added 22.5 mL Acid

Determine the Alkalinity Species and Quantities?

SOLUTION:

$$P = 14.5 \text{ mL}$$

$$T = 22.5 \text{ mL}$$

$$T/2 = 11.25 \text{ mL}$$

$P > T/2$, then, alkalinity are OH^{-1} and CO_3^{-2} , initial pH = 10

$$(\text{OH}^{-1}) \text{ alkalinity} = 2P - T$$

$$(\text{CO}_3^{-2}) \text{ alkalinity} = 2(T - P)$$

(Using Eq'n 8)

$$\begin{aligned} - \text{Total Alkalinity} \left(\frac{\text{mg}}{\text{L}} \text{ as } \text{Ca CO}_3 \right) &= T - \text{Alkalinity} = \\ \frac{\text{mL} (22.5) \times 0.02 \times 50000}{100 \text{ mL}} &= 225 \frac{\text{mg}}{\text{L}} \text{ as } \text{Ca CO}_3 \end{aligned}$$

$$\begin{aligned} - \text{Phenolphthalein Alkalinity} \left(\frac{\text{mg}}{\text{L}} \text{ as } \text{Ca CO}_3 \right) &= P - \text{Alkalinity} \\ \frac{\text{mL} (14.5) \times 0.02 \times 50000}{100 \text{ mL}} &= 145 \frac{\text{mg}}{\text{L}} \text{ as } \text{Ca CO}_3 \text{ CO}_3^{-} \end{aligned}$$

$$(\text{OH}^{-1}) \text{ alkalinity} = 2P - T = 2(145) - 225 = 65 \frac{\text{mg}}{\text{L}} \text{ as } \text{Ca CO}_3 \text{ CO}_3^{-}$$

$$(\text{CO}_3^{-2}) \text{ alkalinity} = 2(T - P) = 2(225 - 145) = 160 \frac{\text{mg}}{\text{L}} \text{ as } \text{Ca CO}_3 \text{ CO}_3^{-}$$

ABSTRACT:

Group	Result of Titration	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity
A	$P = 0$	0	0	T (initial pH < 8.3)
B	$P = 0.5T$	0	2P	0
C	$P = T$	T	0	0
D	$P < 0.5T$	0	2P	T - 2P
E	$P > 0.5T$	2P - T	2(T - P)	0

where

P = amount of acid required to reach 8.3

T = total amount of acid required to reach 4.5

Figure – 9 : Alkalinity Species and Measurements

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Water Quality Control

By

Professor : Majeed M. Ramal

Lecture – 6

Alkalinity

Calculation from alkalinity + pH measurements

- * First calculate OH alkalinity from pH measurement

$$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} \quad (18.6)$$

$$\text{Hydroxide alk.} = 50,000 \times 10^{(\text{pH} - \text{p}K_w)} \quad (18.7)$$

At 25°C, $\text{p}K_w = 14.00$. However, it varies from 14.94 at 0°C to 13.53 at 40°C.

- * Second, make use of the principles of the first procedure to calculate carbonate and bicarbonate alkalinity

$$\text{Carbonate alk.} = 2 (\text{phenol. alk.} - \text{hydroxide alk.}) \quad (18.8)$$

- * Titration from pH 8.3 to 4.5 measures the remaining one half of the carbonate + bicarbonate.

- * or

$$\text{Bicarbonate alk.} = \text{total alk.} - (\text{carbonate alk.} + \text{hydroxide alk.}) \quad (18.9)$$

Alkalinity and acidity are based on the “carbonate system” .

$$[\text{Alk.}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{=3}] + [\text{OH}^-] - [\text{H}^+]$$

(mol/L of H^+ that can be neutralized)

$$(\text{Alk.}) = (\text{HCO}_3^-) + (\text{CO}_3^{=3}) + (\text{OH}^-) - (\text{H}^+)$$

(meq/L of H^+ that can be neutralized)

$$\text{Alk. In mg/L as CaCO}_3 = (\text{Alk.}) \times \text{EW CaCO}_3$$

Example :

$$\text{CO}_3^{=3} = 20 \text{ g/m}^3 \quad \text{HCO}_3^{-3} = 488 \text{ g/m}^3$$

$$\text{OH}^{-} = 0.17 \text{ g/m}^3 \quad \text{Alk.} = ?$$

Ion	MW (g/mole)	EW (g/eq)	(eq/m ³)
CO ₃ ⁼	60	30	20/30=0.67
HCO ₃ ⁻	61	61	488/61=8
OH ⁻	17	17	0.17/17=0.01

$$[\text{H}^+][\text{OH}^-] = K_w$$

$$(\text{OH}^-)(\text{H}^+) = K_w$$

$$[\text{H}^+] = 10^{-14} / (0,01 \times 1/1000 \times 1 \text{ mol/eq})$$

$$= 10^{-9} \text{ mol/L} = 10^{-9} \text{ eq/L} = 10^{-6} \text{ eq/m}^3$$

$$[\text{Alk.}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{=}] + [\text{OH}^-] - [\text{H}^+]$$

$$(\text{Alk.}) = 8,00 + 0,67 + 0,01 - 10^{-6}$$

$$= 8,68 \text{ eq/m}^3$$

$$(8,68 \times 10^{-3} \text{ eq/L}) \times (50000 \text{ mg/eq}) = 434 \text{ mg/L as CaCO}_3$$

Expressing in terms of CaCO₃:

Species A

$$\text{mg/L as CaCO}_3 = (\text{mg/L A})(\text{EW CaCO}_3 / \text{EWA})$$

Example : 10 mg/L Mg²⁺, Mg⁺² = 24,3 mg/L EW

$$\text{Mg}^{+2} = 24,3/2 = 12,15 \text{ Conc of Mg}^{+2} \text{ as CaCO}_3$$

$$(10 \text{ mg/L}) \times ((5000 \text{ mg/meq}) / (12150 \text{ mg/meq Mg}^{+2})) = 41,15 \text{ mg/L as CaCO}_3$$

3. Calculation from equilibrium reactions :

$$[H^+] + \frac{\text{alkalinity}}{50,000} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \quad (18.10)$$

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \quad (18.11)$$

$$\text{Carbonate alkalinity (mg/L as CaCO}_3\text{)} = \frac{50,000[(\text{alkalinity}/50,000) + [H^+] - (K_w/[H^+])]}{1 + ([H^+]/2K_{A2})} \quad (18.12)$$

$$\text{Bicarbonate alkalinity (mg/L as CaCO}_3\text{)} = \frac{50,000[(\text{alkalinity}/50,000) + [H^+] - (K_w/[H^+])]}{1 + (2K_{A2}/[H^+])} \quad (18.13)$$

Application of alkalinity data:

- *Chemical coagulation: excess alkalinity should be present
- *Water softening: important in calculating lime and soda ash requirements
- *Biological processes
- *Industrial wastewaters: Many municipalities prohibit caustic alkalinity to sewers
- *IS KI requires $6 < \text{pH} < 12$

pH changes during aeration of water:

- *Common purpose of aeration is to strip
- *Carbon dioxide $\rightarrow \text{pH} \uparrow$
- *Ammonia
- *VOCs
- *Air content to 0.035 % by volume CO_2
- *Henry 's constant: 1500 mg/L.atm Equilibrium conc. For $\text{CO}_2 = 0.00035 \times 1500 = 0.45 \text{ mg/L}$
- $KA1 = [H^+] [HCO_3^-] / [H_2CO_3]$

If alkalinity= 100 mg/L Aerated until equilibrium of CO₂ in air→pH=8,6

pH changes in the presence of algal blooms:

- * Algae use CO₂ in photosynthesis.
- * Algae can reduce CO₂ conc. below its equilibrium concentrations.
- * During algal blooms pH 10 can be seen
- * Algae can continue to extract CO₂ until inhibitory pH (10-11)
- * As pH increase alkalinity forms change
- * Total alkalinity remains constant unless CaCO₃ precipitation occurs

Boiler waters :

- * Carbondioxide is insoluble in boiling water and removed with steam. → pH ↑ → shift of alkalinity from bicarbonate to carbonate, and carbonate to hydroxide → CaCO₃ precipitate

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Third Class

Water Quality Control

By

Assistant Professor : Majeed M. Ramal

Lecture – 7

Hardness

Hardness

- **Hardness** is the concentration of multivalent **metallic cations** in solution (mg/L), which includes mainly Ca^{2+} and Mg^{2+}
- The units are, like alkalinity, mg/L as CaCO_3
- Hardness is classified as carbonate hardness and non-carbonate hardness, depending upon the anion with which it associated.
- Anions of alkalinity (e.g., CO_3^{2-}) and cations of hardness (e.g., Ca^{2+}) are normally derived from the same carbonate minerals – and this is the reason for the observed general association between alkalinity and hardness

1. **Carbonate hardness** - the portion of total hardness that is chemically equivalent to the CO_3^{2-} and HCO_3^- alkalinity present in the water.
2. **Non-carbonate hardness** - that hardness which is in excess of carbonate hardness; will only occur in water where Total Hardness > alkalinity

Example

- $\text{Ca} = 70 \text{ mg/L}$
- $\text{Mg} = 30 \text{ mg/L}$
- $\text{CO}_3 = 50 \text{ mg/L}$
- Calculate Total Hardness (T . H)
- Sol.
- $\text{Ca} = 70/20 = 3.5 \text{ meq/L} = 3.5 * 50 = 175 \text{ mg/l as } \text{CaCO}_3$
- $\text{Mg} = 30/12 = 2.5 \text{ meq/L} = 2.5 * 50 = 125 \text{ mg/L as } \text{CaCO}_3$
- $\text{CO}_3 = 50/30 = 1.67 = 1.67 * 50 = 83.3 \text{ mg/L as } \text{CaCO}_3$
- $\text{HCO}_3 = 90/61 = 1.47 = 1.47 * 50 = 73.7 \text{ mg/l as } \text{CaCO}_3$
- Total Hardness = $175 + 125 = 300 \text{ mg/L as } \text{CaCO}_3$
- C. H = $[\text{CO}_3] + [\text{HCO}_3] = 83.3 + 73.7 = 157 \text{ mg/L as } \text{CaCO}_3$
- N.C.H = $300 - 157 = 143 \text{ mg/L as } \text{CaCO}_3$
- Carbonate hardness (C.H) = Temporary
- Non- Carbonate hardness (N.C.H) = Permanent

	Case 1 mg/l as CaCO_3	Case 2	Case 3
Ca + Mg	300	400	200
$\text{CO}_3 + \text{HCO}_3$	157	400	300
T . H	300	400	200
C . H	157	400	200
N. C . H	143	0	0

Sources

Caused by the presence of multivalent cations, mostly Ca^{2+} and Mg^{2+} ; (Fe^{2+} , Mn^{2+} , Sr^{2+} , Al^{3+} may be present in much smaller amounts).

Impacts

- Hardness determines how hard or easy it is to lather soap
- **Hard water** is water that requires considerable amounts of soap to produce foam or lather; the precipitates formed by the hardness and soap adheres to surfaces of tubes, sinks and dishwashers, produces scale in hot water pipes, etc.
- Not a health concern, but have **economic concern**

Measurement

Hardness can be measured using chemical titration to determine the quantity of calcium and magnesium ions.

Use

- Analysis for hardness is commonly made on natural waters and on waters for potable supplies and for certain industrial uses.
- Soft < 50 mg/L as CaCO_3
- Moderately hard 50-150 mg/L as CaCO_3
- Hard 150-300 mg/L as CaCO_3
- Very hard >300 mg/L as CaCO_3
- Maximum hardness of 500 mg/L in drinking water (public health service standards)

Fluoride

- Associated in nature with few types of sedimentary or igneous rocks.
- Fluoride is seldom found in surface waters,
- Fluoride appears in groundwater in only few geographical regions,
- Toxic to humans and animals in large quantities,
- Beneficial with small concentrations,
- 1 mg/L concentration in drinking water help to prevent dental cavities in children ... harder, stronger teeth.
- Added to water supplies for good dental formation
- Excessive fluoride can result in discoloration of teeth ($< 2\text{mg/L}$)

Metals

1. Nontoxic Metals

Include calcium, magnesium, sodium, iron, manganese, aluminum, copper and zinc.

Sodium: - in natural waters, earth crust.

- reactive , soluble in water.
- corrosive to metal surfaces,
- Toxic to plants in large concentrations.

Iron and manganese :

- in natural waters,
- (0.3 mg/L and 0.05 mg/L respec.) concentrations cause color problems and may cause taste and odor problems in the presence of some bacteria.

- Iron associate with chloride or bicarbonate or sulfate,
- In the presence of oxygen, Fe^{2+} is oxidized to Fe^{3+} and forms an insoluble compounds with hydroxide ($\text{Fe}(\text{OH})_3$).
- Manganese (Mn^{2+}) associated with chloride or nitrate or sulfate are soluble, while oxidized (Mn^{3+} , Mn^{5+}) are insoluble.

Toxic Metals

- Are harmful to humans and other organisms in small quantities
- include arsenic, barium, cadimuum, chromium, lead, mercury, and silver

ORGANICS

• Biodegradable Organics

Biodegradable materials consists organics that can be utilized for food by naturally occurring microorganisms within a reasonable length of time.

Source of organics

- Organics include fats, proteins, alcohols, acids, aldehydes, and esters.
- Organics are the end product of the initial microbial decomposition of plant or animal tissue.
- Result from domestic or industrial wastewater discharge.

Microbial utilization of dissolved organics can be accompanied by *oxidation* (addition of oxygen to elements of the organic molecule) or by *reduction* (addition of hydrogen).

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Water Quality Control

By

Professor : Majeed M. Ramal

LECTURE 8

SOFTENING

SOFTENING:

Hardness as a water quality parameter discussed in previous Lectures , the term 'reduction of hardness' or " *softening*", is a process commonly practiced in water treatment , *Softening* may be defined as *a Chemical precipitation is among the most common methods used to soften water*

Softening may be done by the water utility at the treatment plant or by the consumer at the point of use, depending on the economics of the situation and the public desire for soft water.

Generally, softening of moderately hard water (50- 150 mg/L Hardness) is best left to the consumer, while harder water should be softened at the water treatment plant . softening processes commonly used are chemical precipitation and Ion exchange, either of which may be employed at the utility-owned treatment plant . Home-use softener are almost exclusively ion-exchange units.

Chemical Precipitation

The different species of hardness have different solubility limits, as shown in Table 4-2. The least soluble forms are calcium carbonate and magnesium hydroxide. Chemical precipitation is accomplished by converting calcium hardness to calcium carbonate and magnesium hardness to magnesium hydroxide. This can be accomplished by the lime-soda ash process or by the caustic soda process.

Lime-soda ash All forms of carbonate hardness as well as magnesium noncarbonate hardness can be converted to the precipitating species by the addition of lime (CaO). In the following equations, the symbol s is used to indicate that a solid precipitate forms and that it is sufficiently dense to settle by gravity.

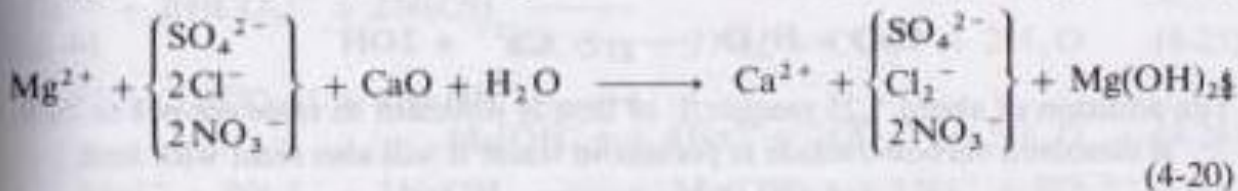
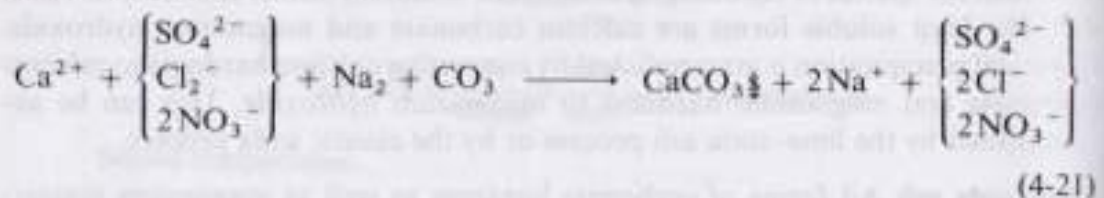


Table 4-2 Equilibrium of solid and dissolved species of common ions

Mineral	Formula	Solubility, mg/L CaCO ₃ at 0°C
Calcium bicarbonate	Ca(HCO ₃) ₂	1,620
Calcium carbonate	CaCO ₃	15
Calcium chloride	CaCl ₂	336,000
Calcium sulfate	CaSO ₄	1,290
Calcium hydroxide	Ca(OH) ₂	2,390
Magnesium bicarbonate	Mg(HCO ₃) ₂	37,100
Magnesium carbonate	MgCO ₃	101
Magnesium chloride	MgCl ₂	362,000
Magnesium hydroxide	Mg(OH) ₂	17
Magnesium sulfate	MgSO ₄	170,000
Sodium bicarbonate	NaHCO ₃	38,700
Sodium carbonate	Na ₂ CO ₃	61,400
Sodium chloride	NaCl	225,000
Sodium hydroxide	NaOH	370,000
Sodium sulfate	Na ₂ SO ₄	33,600

Source: Adapted from Loewenthal and Marais, [4-38]

As seen in Eq. (4-20), removal of magnesium noncarbonate hardness results in the formation of calcium noncarbonate hardness. This calcium noncarbonate hardness, as well as any initially present in the water, can be removed by the addition of soda ash (Na₂CO₃):

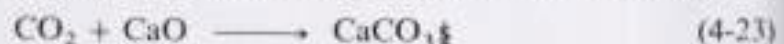


The sodium in Eq. (4-21) is soluble and, unless excessive amounts are added, is permissible in potable water.

The precipitation of CaCO₃ and Mg(OH)₂ is pH-dependent, as is illustrated in Fig. 4-24. The optimum pH for CaCO₃ precipitation by lime addition is from 9 to 9.5, while effective precipitation of Mg(OH)₂ under water-treatment plant conditions requires a pH of about 11.0. Since most natural waters have a pH considerably below these values, it is often necessary to artificially raise the pH. This can be accomplished by the addition of **an excess amount of lime**:



The addition of about 1.25 mequiv/L of lime is sufficient to raise the pH to 11.0. If dissolved carbon dioxide is present in water it will also react with lime.



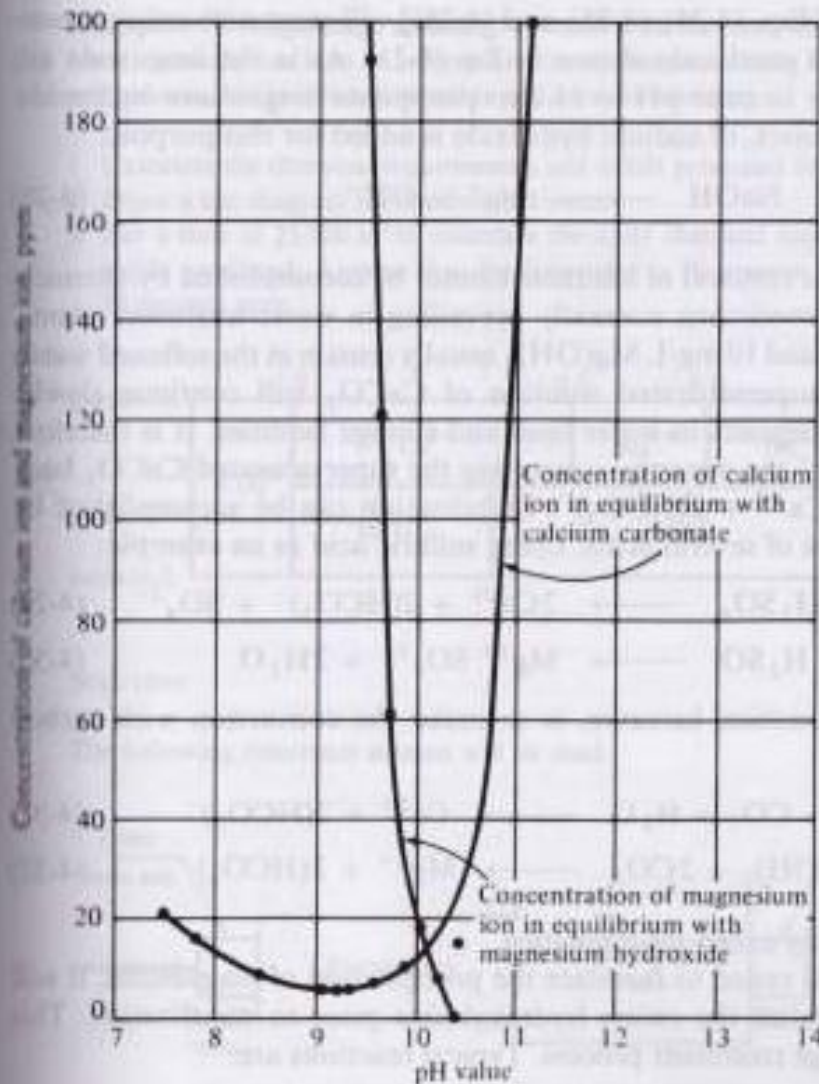
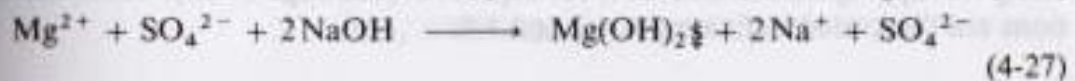
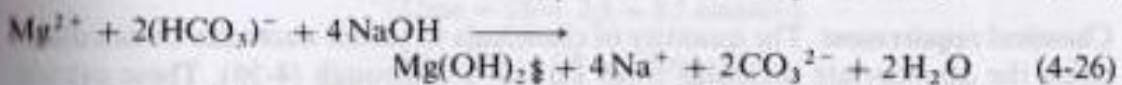
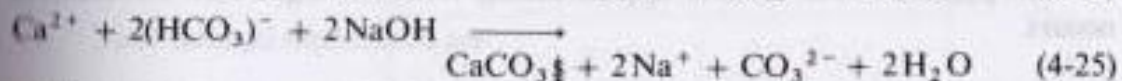


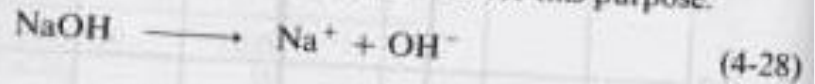
Figure 4-24 Equilibrium concentration of calcium and magnesium ions as a function of pH. (From Powell [4-43].)

Although this reaction does not reduce hardness, it does consume lime. Removal of supersaturated CO_2 by aeration is often practiced to reduce lime requirements. If CO_2 exceeds 10 mg/L it may be economically advantageous to remove it prior to softening.

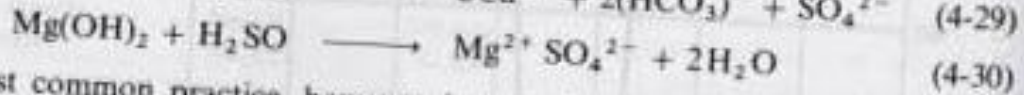
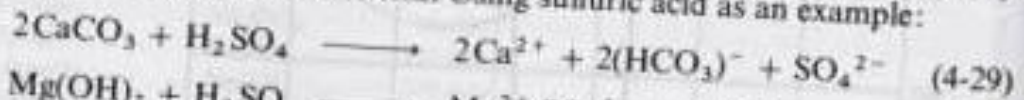
Caustic soda. All forms of hardness can also be converted to the precipitating species by the addition of caustic soda (NaOH).



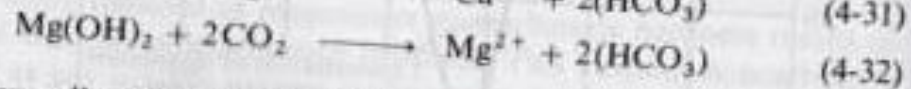
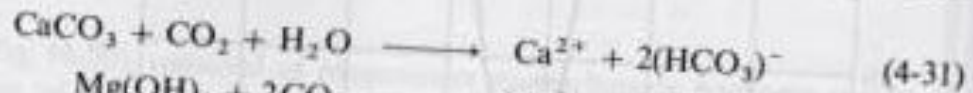
The soda ash formed [Eqs. (4-24), (4-25), and (4-26)] will react with calcium non-carbonate hardness as previously shown in Eq. (4-21). As in the lime-soda ash process, it is necessary to raise pH to 11.0 to precipitate magnesium hydroxide. An excess of 1.25 mequiv/L of sodium hydroxide is added for this purpose.



Stabilization Complete removal of hardness cannot be accomplished by chemical precipitation. Under conditions normally prevailing in water-treatment plants, up to 40 mg/L CaCO_3 and 10 mg/L $\text{Mg}(\text{OH})_2$ usually remain in the softened water. Precipitation of the supersaturated solution of CaCO_3 will continue slowly, however, resulting in deposits in water lines and storage facilities. It is therefore necessary to "stabilize" the water by converting the supersaturated CaCO_3 back to the soluble form, $\text{Ca}^{2+} + 2(\text{HCO}_3)^-$. Stabilization can be accomplished by the addition of any one of several acids. Using sulfuric acid as an example:



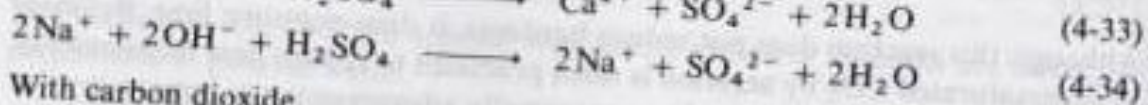
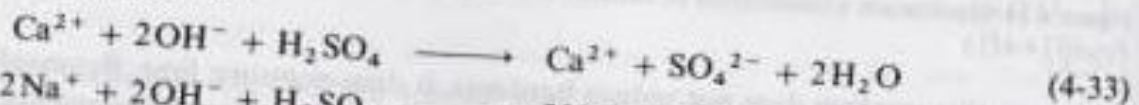
The most common practice, however, is to make the conversion with carbon dioxide:



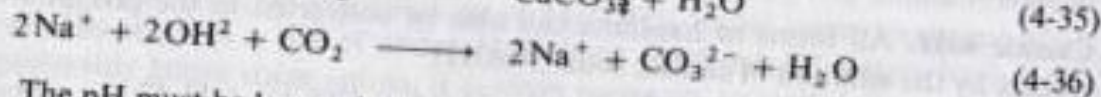
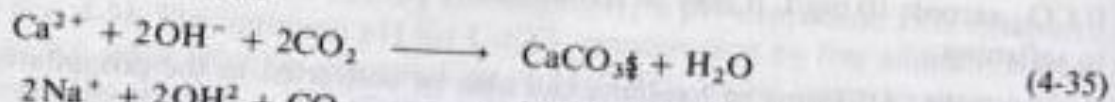
This process is generally called *recarbonation*.

If the pH has been raised to facilitate the precipitation of magnesium, it will be necessary to neutralize the excess hydroxyl ions prior to stabilization. This necessitates a two-stage treatment process. Typical reactions are:

With sulfuric acid



With carbon dioxide

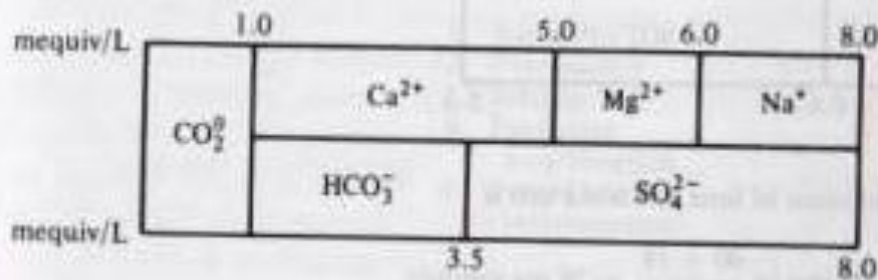


The pH must be lowered to approximately 9.5 before significant stabilization occurs.

Chemical requirement The quantity of chemicals to soften water can be calculated using the appropriate formulas from Eqs. (4-17) through (4-36). These calculations are illustrated in Examples 4-7 and 4-8.

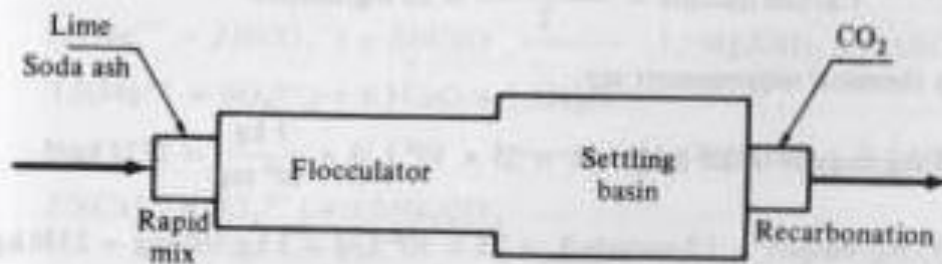
Example 4-7: Single-stage softening A water with the ionic characteristics shown in the bar diagram below is to be softened to the minimum calcium hardness by the lime-soda ash process. Magnesium removal is not deemed necessary.

1. Calculate the chemical requirements and solids produced in milliequivalents per liter.
2. Draw a bar diagram for the finished water.
3. For a flow of 25,000 m³/d, calculate the daily chemical requirement and the mass of solids produced. Assume that the lime used is 90 percent pure and the soda ash is 85 percent pure.

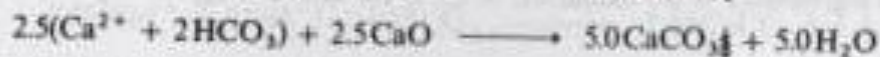


SOLUTION

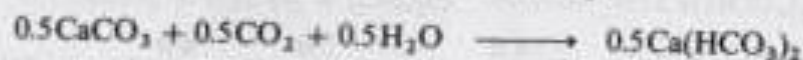
The following treatment scheme will be used.



1. Calculate chemical requirements using appropriate formulas.



Second-stage recarbonation will be required to stabilize the water. Assuming a CaCO₃ concentration of 40 mg/L in the effluent from the settling basin, 25 mg/L should be converted to reach the equilibrium of 15 mg/L of CaCO₃.



Total chemical requirements are:

$$\text{Lime} = 1.0 + 2.5 = 3.5 \text{ mequiv/L}$$

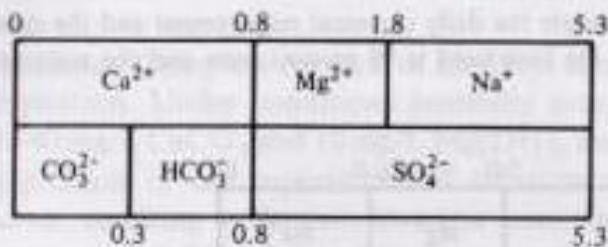
$$\text{Soda ash} = 1.5 = 1.5 \text{ mequiv/L}$$

$$\text{CO}_2 = 0.5 \text{ mequiv/L}$$

Solids produced are

$$\text{CaCO}_3 = 1.0 + 5.0 + 1.5 - 0.8 = 6.7 \text{ mequiv/L}$$

2. The bar diagram for the finished water is



3. The equivalent mass of lime and soda ash is

$$\text{Lime} = \frac{40 + 16}{2} = 28 \text{ mg/mequiv}$$

$$\text{Soda ash} = \frac{2(23) + 12 + 3(16)}{2} = 53 \text{ mg/mequiv}$$

$$\text{Carbon dioxide} = \frac{12 + 2(16)}{2} = 22 \text{ mg/mequiv}$$

The daily chemical requirements are:

$$(1/0.9) 28 \text{ mg/mequiv} \times 3.5 \text{ mequiv/L} \times 25 \times 10^6 \text{ L/d} \times \frac{1 \text{ kg}}{10^6 \text{ mg}} = 2722 \text{ kg/d}$$

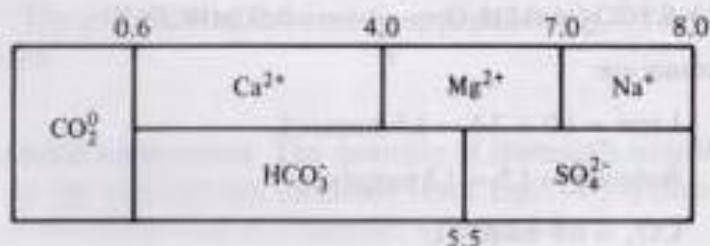
$$(1/0.85) 53 \text{ mg/mequiv} \times 1.5 \text{ mequiv/L} \times 25 \times 10^6 \text{ L/d} \times 1 \text{ kg}/10^6 \text{ mg} = 2338 \text{ kg/d}$$

$$22 \text{ mg/mequiv} \times 0.5 \text{ mequiv/L} \times 25 \times 10^6 \text{ L/d} \times 1 \text{ kg}/10^6 \text{ mg} = 275 \text{ kg/d}$$

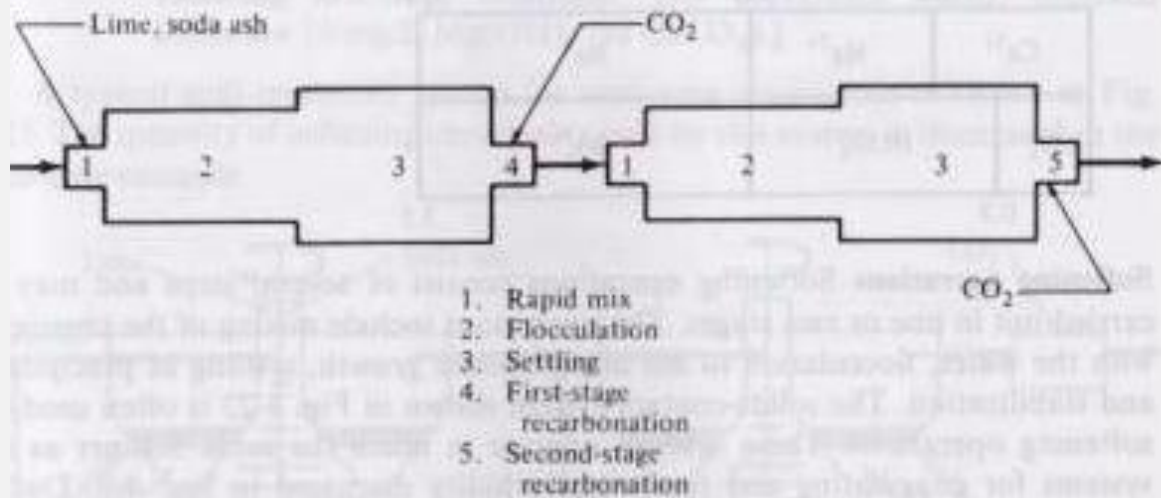
The mass of dry solids produced per day is

$$50 \text{ mg/mequiv} \times 6.7 \text{ mequiv/L} \times 25 \times 10^6 \text{ L/d} \times 1 \text{ kg}/10^6 \text{ mg} = 8375 \text{ kg/d}$$

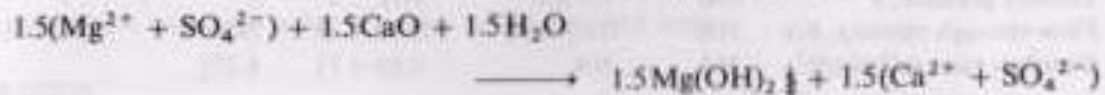
Example 4-8: Two-stage softening A water with the ionic characteristics shown below is to be softened to the minimum possible hardness by the lime-soda-ash-excess-lime process. Calculate the required chemical quantities in milliequivalents per liter. Draw a bar diagram of the finished water.



SOLUTION The following treatment scheme will be used.



1. Calculate chemical quantities using appropriate formulas.



Excess lime = 1.25 mequiv/L

For first-stage recarbonation, use CO_2 to neutralize excess lime.



Assuming 40 mg/L CaCO_3 and 10 mg/L $\text{Mg}(\text{OH})_2$ remaining in solution after second-stage settling.

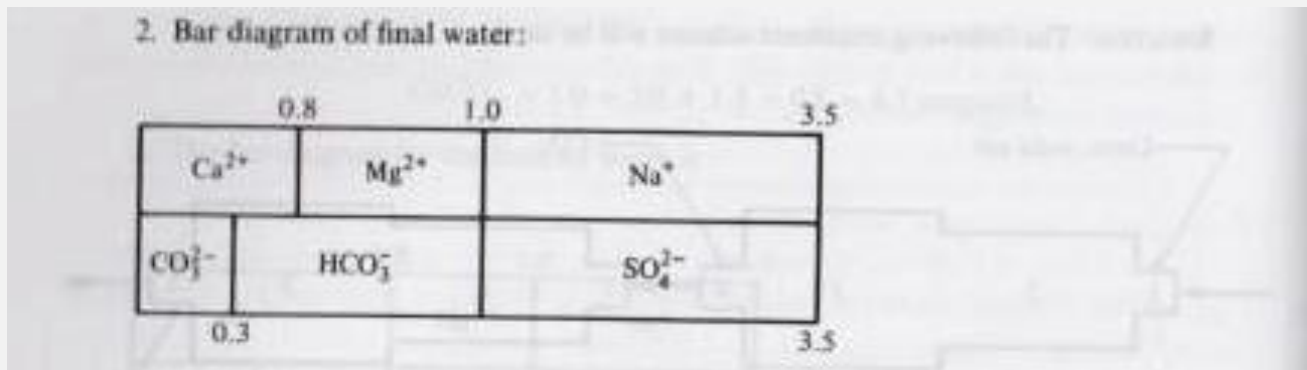


Total chemical quantities are

$$\text{Lime} = 0.6 + 3.4 + 3.0 + 1.5 + 1.25 = 9.75$$

$$\text{Soda ash} = 1.5$$

$$\text{CO}_2 = 1.25 + 0.4 + 0.5 = 2.15$$



Homework:

Two-stage softening: A water with the ionic characteristics shown below is to be softened by the lime-soda-ash-excess-lime process .Calculate the required chemical quantities in (meq/L).Draw a bar diagram of the finished water. For a flow of (5×10^6 . L/d), calculate the daily chemical requirements and the mass of solid produced. Assume that the lime and the soda ash used are (90 %) pure? (15 Marks)

Element	CO ₂	Calcium ⁺²	Magnesium ⁺²	Na ⁺¹	HCO ₃ ⁻¹	SO ₄ ⁻²	Cl ⁻¹
Concentration (mg/L)	8.8	40	14.7	13.7	164.7	29	17.8

Elements	Ca ⁺²	Mg ⁺²	K ⁺¹	Cl ⁻¹	So ₄ ⁻²	Na ⁺¹	Hco ₃ ⁻¹
Atomic Mass	40	24 . 3	39.1	35 . 5	96	23	61

Softening operations Softening operations consist of several steps and may be carried out in one or two stages. The operations include mixing of the chemicals with the water, flocculation to aid in precipitate growth, settling of precipitate, and stabilization. The solids-contact system shown in Fig. 4-23 is often used for softening operations. These systems operate in much the same manner as the systems for coagulating and removing turbidity discussed in Sec. 4-6. Design criteria, however, are slightly different and are summarized in Table 4-3.

Table 4-3 Typical design criteria for softening systems

Parameter	Mixer	Flocculator	Settling basin	Solids-contact basin
Detention time*	5 min	30-50 min	2-4 h	1-4 h
Velocity gradient, s^{-1}	700	10-100	NA	†
Flow-through velocity, ft/s	NA	0.15-0.45	0.15-0.45	NA
Overflow rate, gal/min/ft ²	NA	NA	0.85-1.71	4.27‡

* This should be confirmed by pilot-plant analysis for each water.

† Velocity gradient in mixer and flocculator component should be approximately the same as in flow-through units.

‡ At slurry blanket-clarifier water interface.

Source: Adapted from *Recommended Standards*. [4-44]

Water with high magnesium hardness is often softened by a process called *split treatment*. This process bypasses the first-stage softening unit with a part of the incoming water. Excess lime is added to facilitate the removal of magnesium in the first stage and, instead of being neutralized thereafter, is used to precipitate the calcium hardness in the bypassed water in the second stage. Since no magnesium is removed in the bypassed water, the initial magnesium hardness and the allowable magnesium hardness in the finished water govern the quantity that may be bypassed:

$$Q_x = \frac{Mg_f - Mg_1}{Mg_r - Mg_1} \quad (4-37)$$

where Q_x = fraction of the total flow bypassed

Mg_f = Magnesium concentration in the finished water, 40-50 mg/L (as $CaCO_3$) usually acceptable

Mg_r = magnesium concentration in the raw water, mg/L

Mg_1 = magnesium concentration remaining in the fraction of the water receiving first-stage treatment. [As previously stated, practical limits are 10 mg/L $Mg(OH)_2$ (as $CaCO_3$).]

A typical split-treatment system for removing magnesium is shown in Fig. 4-25. The quantity of softening chemicals saved by this system is illustrated in the following example.

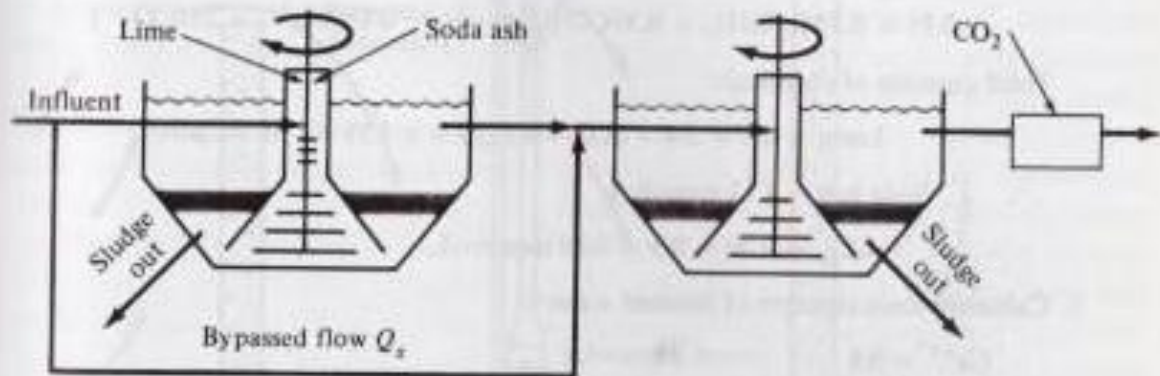


Figure 4-25 Flow diagram for softening by split treatment.

Example 4-9: Softening by split treatment Use split treatment to soften the water with ionic strength given in Example 4-8. Assume that a final hardness of less than 100 mg/L is acceptable, provided the magnesium is less than 45 mg/L. Calculate the chemical requirements and draw a bar diagram of the finished water.

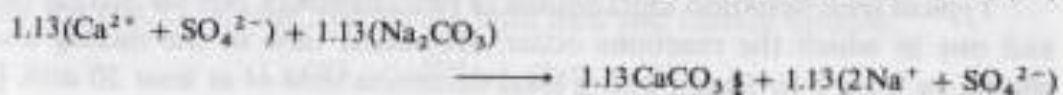
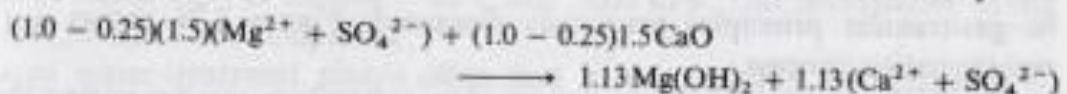
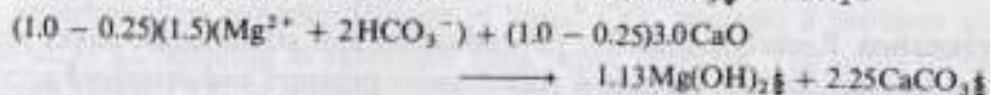
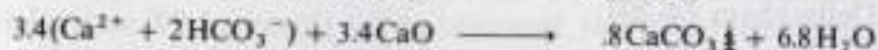
SOLUTION

The treatment scheme shown in Fig. 4-25 will be used.

1. Calculate the bypass fraction:

$$Q_s = \frac{Mg_r - Mg_1}{Mg_r - Mg_1} = \frac{0.9 - 0.2}{3.0 - 0.2} = 0.25$$

2. Calculate the quantity of chemicals added to first stage:



Check to make sure extra lime is enough to provide 1.25 mequiv/L:

$$\frac{(0.6 + 3.4)0.25}{0.75} = 1.33$$

1.33 > 1.25, so acceptable

For second-stage recarbonation:



Total quantity of chemicals:

$$\text{Lime} = 0.6 + 3.4 + (1.0 - 0.25)(3.0 + 1.5) = 7.38 \text{ mequiv/L}$$

$$\text{Soda ash} = 1.13 \text{ mequiv/L}$$

$$\text{CO}_2 = 0.30 + 0.5 = 0.80 \text{ mequiv/L}$$

3. Calculate ionic strength of finished water:

$$\text{Ca}^{2+} = 0.8$$

$$\text{Mg}^{2+} = 0.75 \times 0.2 \text{ (first stage)} + 0.25 \times 3.0 \text{ (in bypass)} = 0.9$$

$$\text{Na}^+ = 1.0 + 1.13 = 2.13$$

$$\text{CO}_3^{2-} = 0.3$$

$$\begin{aligned} \text{HCO}_3^- &= 0.5(\text{conversion of CaCO}_3) + 0.15(\text{conversion of Mg}(\text{OH})_2) \\ &\quad + 0.25 \times 1.5 \text{ (associated with by passed Mg)} = 1.03 \end{aligned}$$

$$\text{SO}_4^{2-} = 2.5$$

0.8		1.70		3.83
Ca ²⁺		Mg ²⁺		Na
CO ₃ ²⁻	HCO ₃ ⁻	SO ₄ ²⁻		
0.3	1.33	3.83		

For a more complete description of split treatment, the reader is referred to Cleasby and Dellingham. [4-20]

Recarbonation Recarbonation for pH reduction and stabilization takes place in a closed reactor. Carbon dioxide is added under pressure and dissolved according to gas-transfer principles previously discussed. Figure 4-26 shows a typical recarbonation process.

Typical recarbonation units consist of two chambers, one for mixing the CO₂ and one in which the reactions occur. Detention time in the mixing chamber should be from 3 to 5 min, with a total detention time of at least 20 min. [4-44]

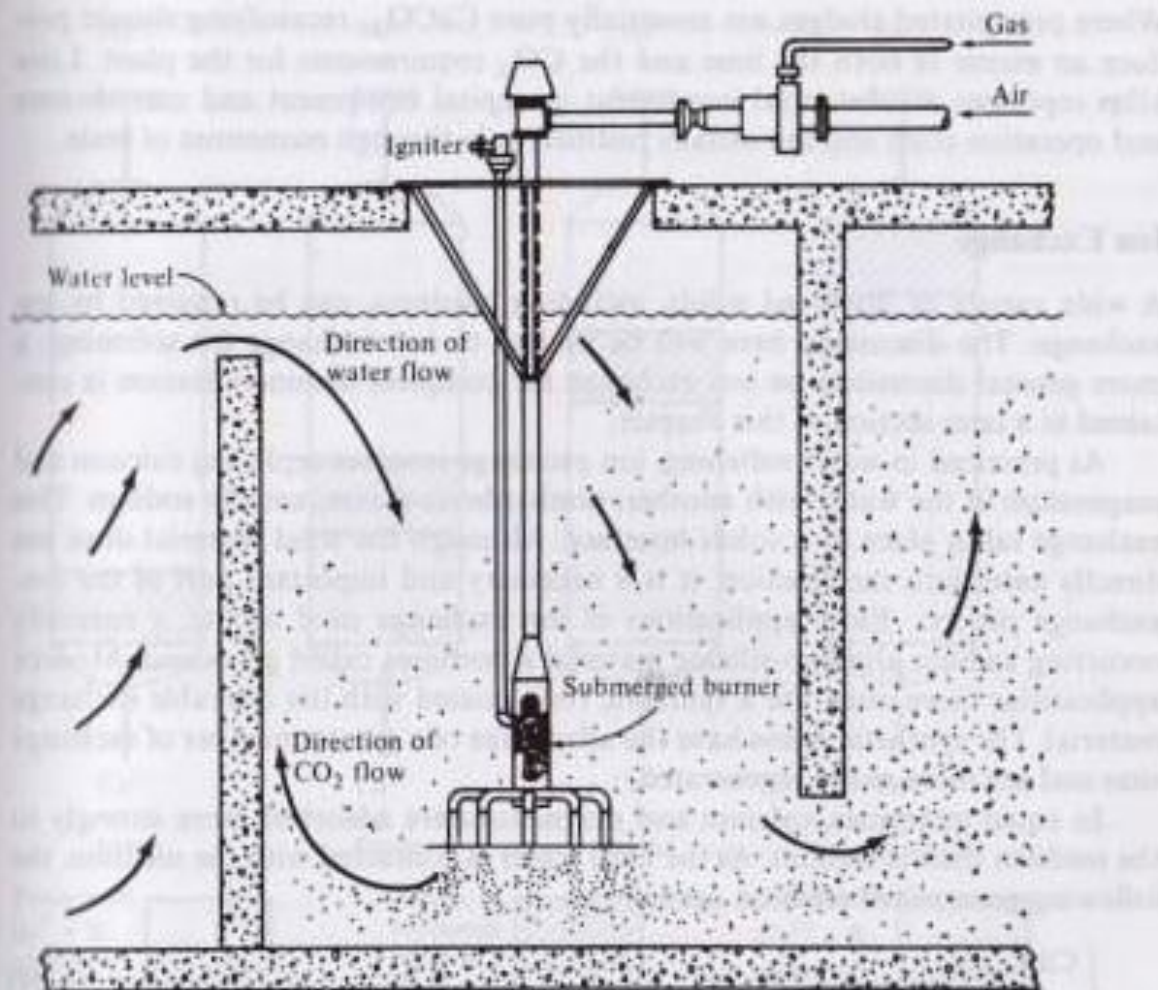
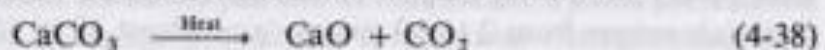


Figure 4-26 Submerged burner for recarbonation. (Courtesy of Ozark-Mahoning Company.)

Where split treatment is employed it may be necessary to follow the recarbonation unit with a settling chamber if the influent to the units still contains an excess of lime. [4-45] All recarbonation units should have provisions for periodic cleaning as some precipitate will accumulate.

The source of CO_2 may be the exhaust from combustion of natural gas ($\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$) or CO_2 which has been purified and shipped to the plant in containers. Walker [4-58] suggests that the stoichiometric quantity of CO_2 be multiplied by a factor of 2 to compensate for inefficiency of CO_2 transfer from the exhaust gases if submerged burners are used. Liquefied CO_2 that is essentially pure (99.5 percent) can be obtained; this greatly enhances the efficiency of the recarbonation process. Storage of liquid CO_2 presents a problem since it gasifies at 31°C , resulting in extremely high vapor pressure. The usual procedure is to store liquid CO_2 at around -20°C and 2000 kPa. This necessitates strong tanks and refrigeration equipment.

Large water-treatment plants often find it economically advantageous to recalcify the CaCO_3 sludge, recovering both lime and carbon dioxide.



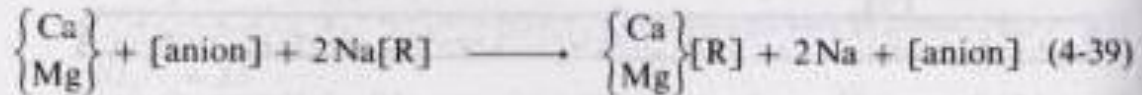
Where precipitated sludges are essentially pure CaCO_3 , recalcifying should produce an excess of both the lime and the CO_2 requirements for the plant. Lime kilns represent a substantial investment in capital equipment and maintenance and operation costs and are usually justified only through economies of scale.

Ion Exchange

A wide variety of dissolved solids, including hardness, can be removed by ion exchange. The discussion here will be limited to ion exchange for softening; a more general discussion on ion exchange for complete demineralization is contained in a later section of this chapter.

As practiced in water softening, ion exchange involves replacing calcium and magnesium in the water with another, nonhardness cation, usually sodium. This exchange takes place at a solids interface. Although the solid material does not directly enter into the reaction, it is a necessary and important part of the ion-exchange process. Early applications of ion exchange used zeolite, a naturally occurring sodium alumino-silicate material sometimes called *greensand*. Modern applications more often use a synthetic resin coated with the desirable exchange material. The synthetic resins have the advantage of a greater number of exchange sites and are more easily regenerated.

In equal quantities, calcium and magnesium are adsorbed more strongly to the medium than is sodium. As the hard water is contacted with the medium, the following generalized reaction occurs.



The reaction is virtually instantaneous and complete as long as exchange sites are available. The process is depicted graphically in Fig. 4-27.

When all of the exchange sites have been utilized, hardness begins to appear in the effluent. Referred to as *breakthrough*, this necessitates the regeneration of the medium by contacting it with a strong sodium-chloride solution. The strength of the solution overrides the selectivity of the adsorption site, and calcium and magnesium are removed and replaced by the sodium.



The system can again function as a softener according to Eq. (4-39).

The capacity and efficiency of ion-exchange softeners vary with many factors, including type of solid medium, type of exchange material used for coating, quantity of regeneration materials, and regeneration contact time. The overall quality of the water to be softened is also an important factor. A complete discussion of these factors is beyond the scope of this text and the reader is referred to Refs. [4-47] and [4-53] for greater details. Generally, the capacity of ion-exchange materials ranges from 2 to 10 mequiv/g or about 15 to 100 kg/m³. Regeneration

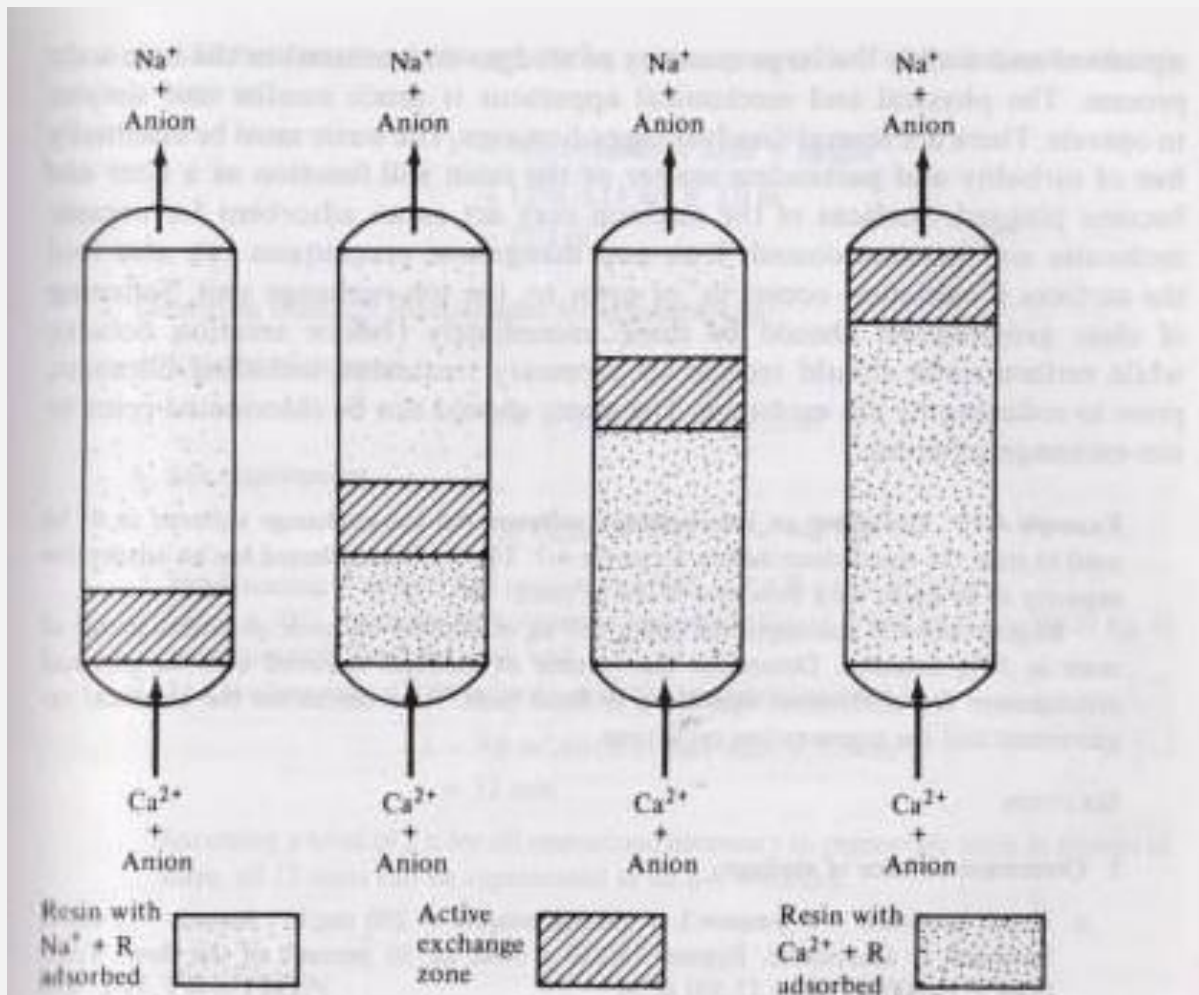


Figure 4-27 Ion-exchange process.

is accomplished using from 80 to 160 kg of sodium chloride per cubic meter of resin in 5 to 20% solution at a flow rate of about 40 L/min · m².

The effluent from the regeneration cycle will contain the hardness accumulated during the softening cycle as well as excess sodium chloride. After regeneration, the medium should be flushed with softened water to remove the excess sodium chloride. These highly mineralized waters constitute a waste stream that must be disposed of properly.

Ion-exchange operations are usually conducted in enclosed structures containing the medium. Water is forced through the material under pressure at up to 0.4 m³/min · m². Single or multiple units may be used and the medium may be contained in either a fixed or a moving bed. Where continuous operation is necessary, multiple units or moving beds are used. Single-stage fixed beds can be used when the flow of treated water can be interrupted for regeneration. Most treatment-plant operations are of the continuous type, while home softeners are serviced intermittently.

Ion-exchange softening at water-treatment plants is becoming more commonplace as more efficient resins are developed and as the process is better understood by design engineers. Ion exchange produces a softer water than chemical pre-

precipitation and avoids the large quantity of sludges encountered in the lime-soda process. The physical and mechanical apparatus is much smaller and simpler to operate. There are several disadvantages, however. The water must be essentially free of turbidity and particulate matter or the resin will function as a filter and become plugged. Surfaces of the medium may act as an adsorbent for organic molecules and become coated. Iron and manganese precipitates can also foul the surfaces if oxidation occurs in, or prior to, the ion-exchange unit. Softening of clear groundwater should be done immediately (before aeration occurs), while surface water should receive all necessary treatment, including filtration, prior to softening by ion exchange. The water should not be chlorinated prior to ion-exchange softening.

Example 4-10: Designing an ion-exchange softener An ion-exchange softener is to be used to treat the water described in Example 4-7. The medium selected has an adsorptive capacity of 90 kg/m^3 at a flow rate of $0.4 \text{ m}^3/\text{min} \cdot \text{m}^2$.

Regeneration is accomplished using 150 kg of sodium chloride per cubic meter of resin in 10% solution. Determine the volume of medium required and the physical arrangement for continuous operation in fixed beds. Also determine the chemical requirement and the regeneration cycle time.

SOLUTION

1. Determine volume of medium.

a. Total hardness = $6 \text{ mequiv/L} \times 50 \text{ mg/mequiv} = 250 \text{ mg/L}$. Assume 75 mg/L hardness is acceptable. Bypass $75/250 = 0.30$, or 30 percent of the flow. Treat $0.70 \times 25,000 \text{ m}^3/\text{d}$, or $17,500 \text{ m}^3/\text{d}$.

b. Hardness to be removed:

$$5.0 \text{ equiv/m}^3 \times 17,500 \text{ m}^3/\text{d} \times 50 \text{ gm/equiv} \times 1 \text{ kg}/10^3 \text{ gm} = 4375 \text{ kg/d}$$

c. Volume of medium for 1-d operation:

$$4375 \text{ kg/d} \times 1 \text{ m}^3/90 \text{ kg} = 48.6 \text{ m}^3 \text{ medium/d operation}$$

2. Determine surface area and height of medium.

a. $17,500 \text{ m}^3/\text{d} \times \text{d}/1440 \text{ min} = 12.15 \text{ m}^3/\text{min}$

$$\text{Area} = 12.15 \text{ m}^3/\text{min} \times \text{min}/0.4 \text{ m} = 30.38 \text{ m}^2$$

b. Use tanks 2.0 m in diameter.

$$A = \pi d^2/4 = 3.14 \text{ m}^2$$

$$\text{No. of tanks} = \frac{30.38}{3.14} = 9.67; \text{ use 9 tanks.}$$

c.

$$\text{Height of medium} = \frac{\text{total volume}}{\text{total area}}$$

$$= \frac{48.6 \text{ m}^3}{9 \times 3.14 \text{ m}^2}$$

$$= 1.72 \text{ m, say } 2 \text{ m}$$

- d. Add three extra tanks for use during regeneration cycle. Total volume of exchange resin is:

$$\begin{aligned} V &= \text{No. of tanks} \times \text{area} \times \text{height} \\ &= 12 \times 3.14 \text{ m}^2 \times 2.0 \text{ m} \\ &= 75.4 \text{ m}^3 \end{aligned}$$

3. Determine chemical requirements for regenerations.

- a. Volume of one unit

$$V = 3.14 \times 2.0 = 6.28 \text{ m}^3$$

- b. Salt requirement

$$150 \text{ kg/m}^3 \times 6.28 \text{ m}^3 = 942 \text{ kg}$$

Regenerating 9 units/d will require $9 \times 942 = 8,478 \text{ kg/d}$ of NaCl.

- c. Using a 10% solution, the volume of regenerate liquid is $942 \text{ kg}/0.1 = 9,420 \text{ kg}$, or approximately 9 m^3 for each unit.

- d. At a loading rate of $0.04 \text{ m}^3/\text{m}^2 \cdot \text{min}$, the regeneration time is

$$\begin{aligned} t &= 9.0 \text{ m}^3 / (0.04 \text{ m}^3/\text{m}^2 \cdot \text{min} \times 3.14 \text{ m}^2) \\ &= 72 \text{ min} \end{aligned}$$

Assuming a total of 2 h for all operations necessary to regenerate units in groups of three, all 12 units can be regenerated in an 8-h workday.

Iraq Republic of
Ministry of Higher Education and Scientific Research
University of Anbar
College of Engineering
Dams And Water Resources Department

Third Class

Water Quality Control

By

Professor : Majeed M. Ramal

Lecture – 9-2

DO Sag Curve Modeling

SELF PURIFICATION OF NATURAL STREAMS

The self purification of natural water systems is a complex process that often involves physical, chemical, and biological processes working simultaneously. The amount of dissolved Oxygen (DO) in water is one of the most commonly used indicators of a river health. As DO drops below 4 or 5 mg/L the forms of life that can survive begin to be reduced. A minimum of about 2.0 mg/L of dissolved oxygen is required to maintain higher life forms. A number of factors affect the amount of DO available in a river. Oxygen demanding wastes remove DO; plants add DO during day but remove it at night; respiration of organisms removes oxygen. In summer, rising temperature reduces solubility of oxygen, while lower flows reduce the rate at which oxygen enters the water from atmosphere.

Factors Affecting Self Purification :

1. **Dilution**: When sufficient dilution water is available in the receiving water body, where the wastewater is discharged, the DO level in the receiving stream may not reach to zero or critical DO due to availability of sufficient DO initially in the river water before receiving discharge of wastewater.
2. **Current**: When strong water current is available, the discharged wastewater will be thoroughly mixed with stream water preventing deposition of solids. In small current, the solid matter from the wastewater will get deposited at the bed following decomposition and reduction in DO.
3. **Temperature**: The quantity of DO available in stream water is more in cold temperature than in hot temperature. Also, as the activity of microorganisms is more at the higher temperature, hence, the self-purification will take less time at hot temperature than in winter.
4. **Sunlight**: Algae produces oxygen in presence of sunlight due to photosynthesis. Therefore, sunlight helps in purification of stream by adding oxygen through photosynthesis.
5. **Rate of Oxidation**: Due to oxidation of organic matter discharged in the river DO depletion occurs. This rate is faster at higher temperature and low at lower temperature. The rate of oxidation of organic matter depends on the chemical composition of organic matter.

Oxygen Sag Analysis :

The oxygen sag or oxygen deficit in the stream at any point of time during self purification process is the difference between the saturation DO content and actual DO content at that time. Oxygen deficit, $D = \text{Saturation DO} - \text{Actual DO}$ The saturation DO value for fresh water depends upon the temperature and total dissolved salts present in it; and its value varies from 14.62 mg/L at 0°C to 7.63 mg/L at 30°C, and lower DO at higher temperatures. The DO in the stream may not be at saturation level and there may be initial oxygen deficit 'D_o'. At this

stage, when the effluent with initial BOD load L_0 , is discharged in to stream, the DO content of the stream starts depleting and the oxygen deficit (D) increases. The variation of oxygen deficit (D) with the distance along the stream, and hence with the time of flow from the point of pollution is depicted by the 'Oxygen Sag Curve' (Figure 1). The major point in sag analysis is point of minimum DO, i.e., maximum deficit. The maximum or critical deficit (D_c) occurs at the inflexion points of the oxygen sag curve.

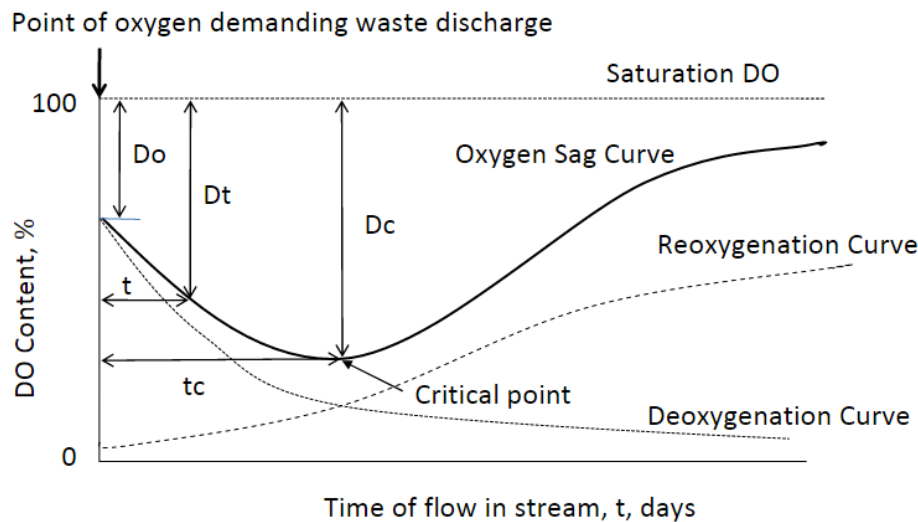
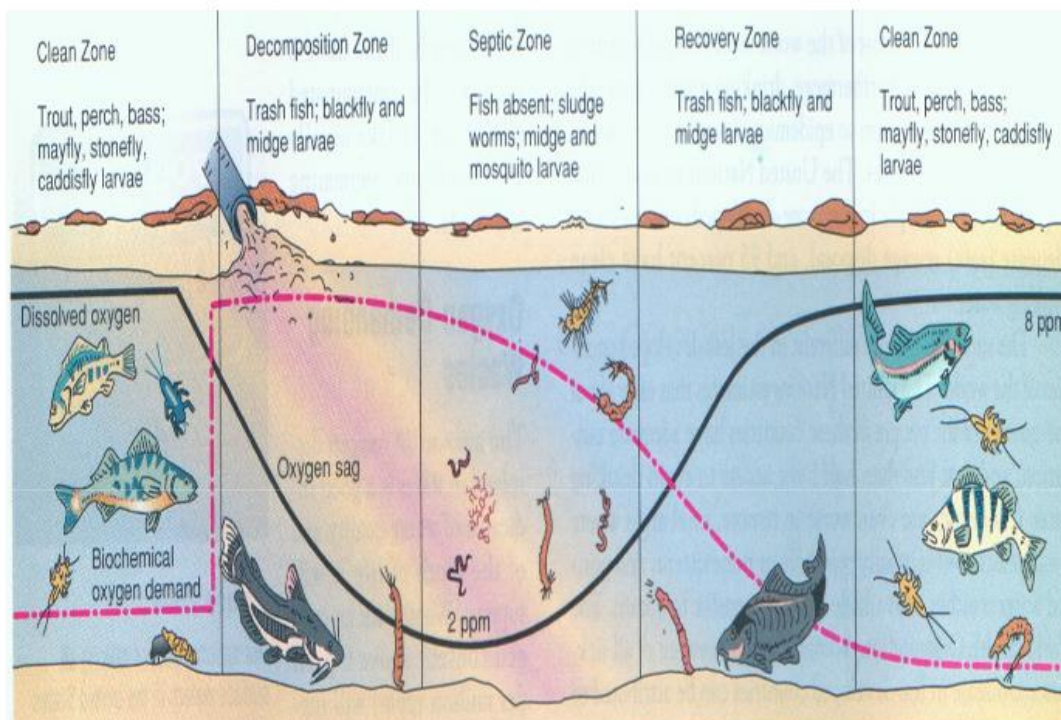


Figure 1 Deoxygenation, reoxygenation and oxygen sag curve

Deoxygenation and Reoxygenation Curves



(Source: Environmental Science: A Global Concern, 3rd ed. by W.P. Cunningham and B.W. Saigo, WC Brown Publishers, © 1995)

Dissolved Oxygen Depletion

When wastewater is discharged in to the stream, the DO level in the stream goes on depleting. This depletion of DO content is known as deoxygenation. The rate of deoxygenation depends upon the amount of organic matter remaining (L_t), to be oxidized at any time t , as well as temperature (T) at which reaction occurs. The variation of depletion of DO content of the stream with time is depicted by the deoxygenation curve in the absence of aeration. The ordinates below the deoxygenation curve (Figure 1) indicate the oxygen remaining in the natural stream after satisfying the bio-chemical demand of oxygen. When the DO content of the stream is gradually consumed due to BOD load, atmosphere supplies oxygen continuously to the water, through the process of re-aeration or reoxygenation, i.e., along with deoxygenation, re-aeration is continuous process. The rate of reoxygenation depends upon:

- i) Depth of water in the stream: more for shallow depth.
- ii) Velocity of flow in the stream: less for stagnant water.
- iii) Oxygen deficit below saturation DO: since solubility rate depends on difference between saturation concentration and existing concentration of DO.
- iv) Temperature of water: solubility is lower at higher temperature and also saturation concentration is less at higher temperature.

Mathematical analysis of Oxygen Sag Curve:

Streeter – Phelps equation The analysis of oxygen sag curve can be easily done by superimposing the rates of deoxygenation and reoxygenation as suggested by the Streeter – Phelps analysis. The rate of change in the DO deficit is the sum of the two reactions as explained below:

$dD_t / dt = f$ (deoxygenation and reoxygenation)

$$\text{OR } dD_t / dt = K_1 L_t - R_2 D_t \dots\dots\dots(1)$$

Where, D_t = DO deficit at any time t ,

L_t = amount of first stage BOD remaining at any time t

K_1 = BOD reaction rate constant or deoxygenation constant (to the base e)

R_2 (or K_2) = Reoxygenation constant (to the base e)

t = time (in days)

dD_t / dt = rate of change of DO deficit Now,

$$L_t = L_0 \cdot e^{-k_1 t}$$

Where, L_0 = BOD remaining at time $t = 0$

Hence,

$$\frac{dDt}{dt} = K' Lo.e^{-K't} - R' Dt \quad \dots(2)$$

or $\frac{dDt}{dt} + R' Dt = K' Lo.e^{-K't} \quad \dots(3)$

This is first order first degree differential equation and solution of this equation is as under

$$Dt = \frac{K' Lo}{R' - K'} [e^{-K't} - e^{-R't}] + Do.e^{-R't} \quad \dots(4)$$

Changing base of natural log to 10 the equation can be expressed as:

$$Dt = \frac{KLo}{R - K} [10^{-K.t} - 10^{-R.t}] + Do.10^{-R.t} \quad \dots(5)$$

Where, K = BOD reaction rate constant, to the base 10

R or (K₂) = Reoxygenation constant to the base 10

Do = Initial oxygen deficit at the point of waste discharge at time t = 0

t = time of travel in the stream from the point of discharge = x/u

x = distance along the stream u = stream velocity

This is Streeter-Phelps oxygen sag equation. The graphical representation of this equation is shown in Figure 2.

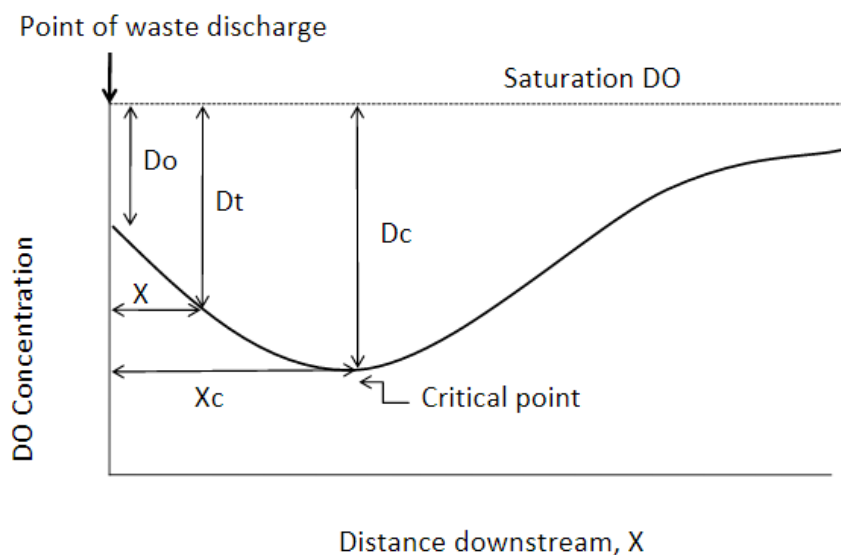
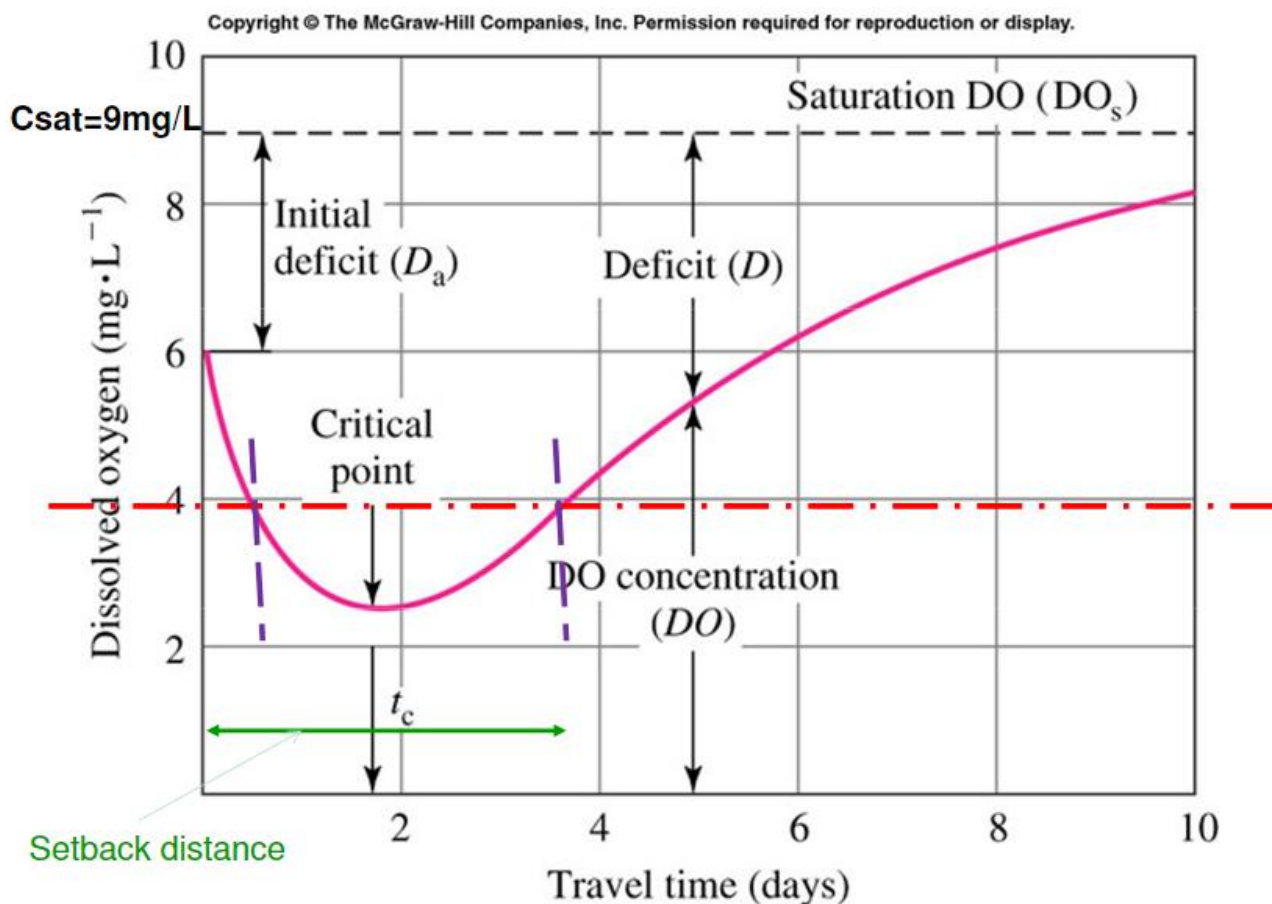


Figure .2 Oxygen sag curve of Streeter-Phelps equation

Note: Deoxygenation and reoxygenation occurs simultaneously. After critical point, the rate of re-aeration is greater than the deoxygenation and after some distance the DO will reach to original level and stream will not have any effect due to addition of wastewater. At time t=0 at x = 0.

Modeling DO in a River

- To model all the effects and their interaction is a difficult task
- The simplest model focuses on two processes:
 - The removal of oxygen by microorganisms during biodegradation (de-oxygenation)
 - The replenishment of oxygen at the interface between the river and the atmosphere (re-aeration)



Critical time and Critical DO deficit

Critical Point = point where stream conditions are at their worst

Determination of Critical DO deficit (Dc) and distance Xc The value of Dc can be obtained by putting $dD/dt = 0$ in equation 3, Hence,

$$D_c = \frac{K'}{R'} L_o . e^{-K' t_c} \quad \dots(6)$$

OR

$$D_c = \frac{K}{R} L_o . 10^{-K . t_c} \quad \dots(7)$$

Where, t_c is time required to reach the critical point. The value of t_c can be obtained by differentiating equation 4 (or 5) with respect to t and setting $dD/dt = 0$ Therefore,

$$t_c = \frac{1}{R' - K'} \log_e \frac{R'}{K'} \left[1 - \frac{D_o(R' - K')}{K' L_o} \right] \quad \dots(8)$$

OR

$$t_c = \frac{1}{R - K} \log_{10} \frac{R}{K} \left[1 - \frac{D_o(R - K)}{K L_o} \right] \quad \dots(9)$$

$$t_c = \frac{1}{k_r - k_d} \ln \left[\frac{k_r}{k_d} \left(1 - D_a \frac{k_r - k_d}{k_d L_a} \right) \right]$$

L_a : ultimate BOD after mixing

The distance X_c is given by $X_c = t_c \cdot u$ Where, u = velocity of flow in the stream The deoxygenation constant K , is obtained by laboratory test or field tests, and varies with temperature as given below:

$$K_T = K_{20}(\theta)^{T-20} \quad \dots(10)$$

Where, $\theta = 1.047$

The reoxygenation constant R or (K_2) also varies with the temperature and can be expressed as: $R_T = R_{20}(\theta)^{T-20} \quad \dots(11)$

Where, $\theta = 1.016$

Where, $R = 0.15$ to 0.20 for low velocity large stream = 0.20 to 0.30 for normal velocity large stream , and 0.10 to 0.15 for lakes and sluggish stream.

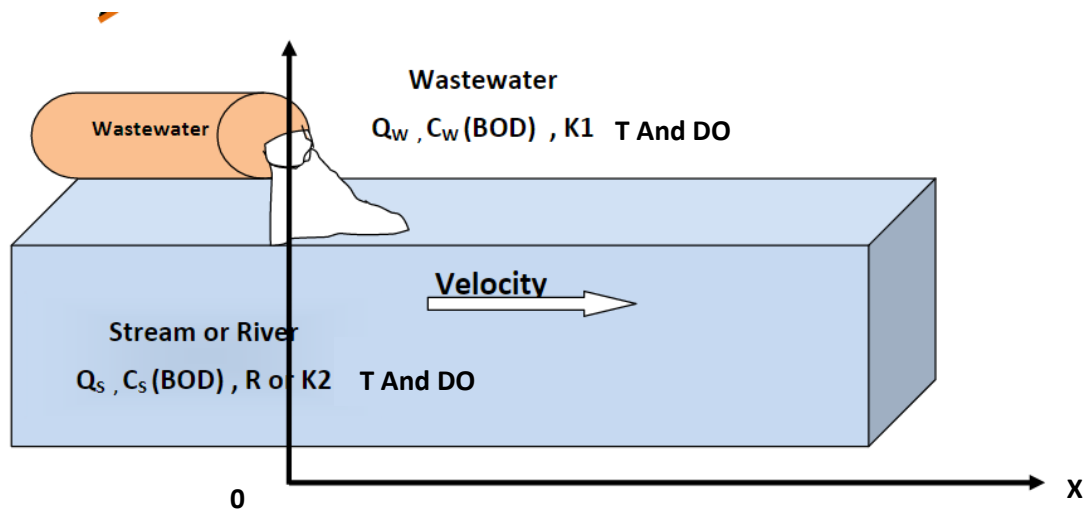
Example : 1

A city discharges 20000 m³/day of sewage into a river whose rate of flow is 0.7 m³/sec.

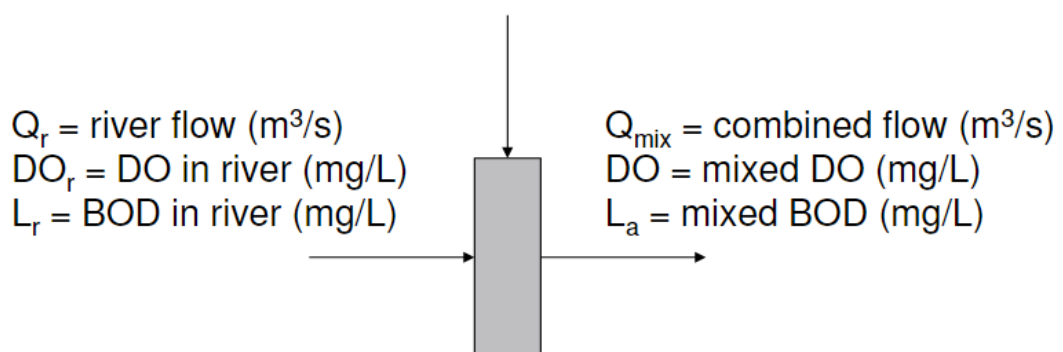
Determine D.O. deficit profile for 100 km from the following data:

River	Sewage effluent from STP
5 day B.O.D. at 20°C = 3.4 mg/l	5 day B.O.D. at 20°C = 45 mg/l
Temperature 23°C	Temperature 26°C
D.O. = 8.2 mg/l	D.O. = 2.0 mg/l

Velocity of mix = 0.25 m/sec, R'=0.4, K' = 0.23



Q_w = waste flow (m³/s)
 DO_w = DO in waste (mg/L)
 L_w = BOD in waste (mg/L)



Dilution Equation (Mass Balance Equation)=

$$C_{mixture} = \frac{Q_r C_r + Q_w C_w}{Q_r + Q_w = Q_{TOTAL}}$$

This equation used to measure all variables after mixing

Solution

Saturation value of D.O. at 23.74 °C deg is 8.57 mg/l

River discharge = 0.7 m³/sec, Sewage discharge = 20000/(24x 3600) = 0.231 m³/sec

$$\text{BOD of mix} = \frac{(0.7 \times 3.4 + 0.231 \times 45)}{(0.7 + 0.231)} = 13.72 \text{ mg/l}$$

$$\text{D.O. of mix} = \frac{(0.7 \times 8.2 + 0.231 \times 2.0)}{(0.7 + 0.231)} = 6.66 \text{ mg/l}$$

$$\text{Temp. of mix} = \frac{(0.7 \times 23 + 0.231 \times 26)}{(0.7 + 0.231)} = 23.74 \text{ }^{\circ}\text{C}$$

$$\text{Ultimate B.O.D. } L_t = L_0 (1 - e^{-kxt})$$

$$13.72 = L_0 (1 - e^{-0.23 \times 5})$$

$$L_0 = 20.08 \text{ mg/L}$$

$$\text{Initial D.O. deficit } (D_0) = 8.57 - 6.66 = 1.91 \text{ mg/L}$$

Deoxygenation and reoxygenation coefficients at 23.74 °C temperature

$$K_T = K_{20} (\theta)^{T-20} \text{ Hence, } K_{23.74} = 0.23 (1.047)^{23.74-20} = 0.273 \text{ day}^{-1}$$

$$R_T = R_{20} (\theta)^{T-20} \text{ Hence, } R_{23.74} = 0.40 (1.016)^{23.74-20} = 0.424 \text{ day}^{-1}$$

$$\begin{aligned} \text{Critical time } t_c &= \frac{1}{R' - K'} \log_e \frac{R'}{K'} \left(1 - \frac{D_0 \times (R' - K')}{K' \times L_0} \right) \\ &= \frac{1}{0.424 - 0.273} \log_e \frac{0.424}{0.273} \left(1 - \frac{1.91 \times (0.424 - 0.273)}{0.273 \times 20.08} \right) \\ &= 2.557 \text{ days.} \end{aligned}$$

$$\begin{aligned} \text{Critical D.O. deficit, } D_c &= \frac{K'}{R'} L_0 e^{-K' \cdot t_c} \\ &= \frac{0.273}{0.424} 20.08 e^{-0.273 \times 2.557} \\ &= 6.432 \text{ mg/l} \end{aligned}$$

Distance at which it occurs = $L = \text{velocity} \times \text{time}$

$$= (0.25 \text{ m/sec}) \times (2.557 \times 24 \times 60 \times 60 \text{ sec})$$

$$= 55231 \text{ m} = 55.23 \text{ km}$$

Similarly time required for mix to reach at 20 km distance, $t_{20\text{km}} = \frac{(20 \times 1000)}{(0.25 \times 24 \times 3600)}$

$$= 0.926 \text{ day}$$

And DO deficit at 20 km can be calculated using equation 4

$$Dt = \frac{K' Lo}{R' - K'} [e^{-K't} - e^{-R't}] + Do.e^{-R't}$$

Where, $K' = 0.273 \text{ d}^{-1}$, $R' = 0.424 \text{ d}^{-1}$, $Do = 1.91 \text{ mg/L}$ and $Lo = 20.08 \text{ mg/L}$ and $t = 0.926 \text{ day}$

Hence, DO deficit at 20 km = 4.970 mg/L

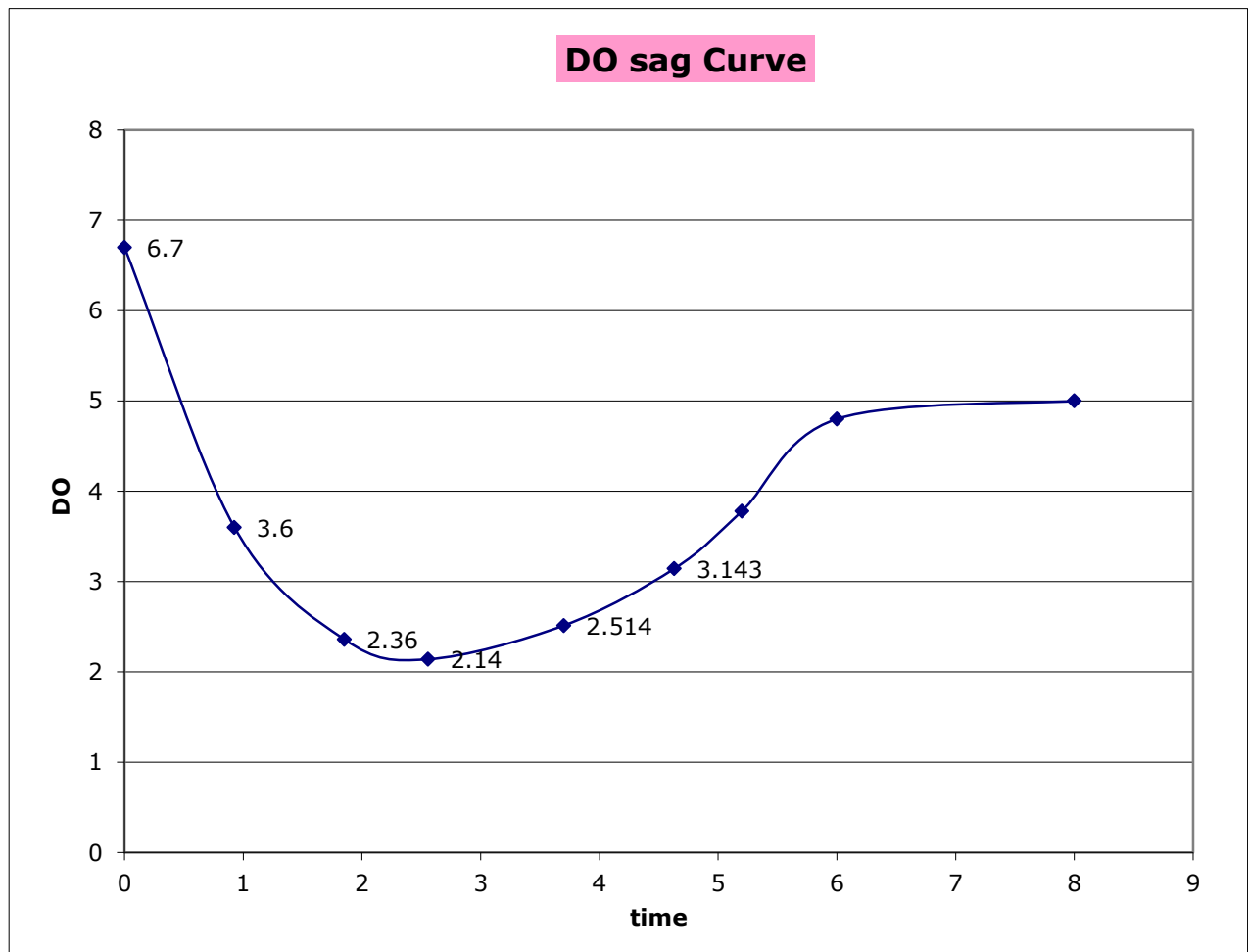
Similarly DO deficit at 40 km (i.e. $t = 1.852 \text{ days}$) = 6.211 mg/L

and DO deficit at 80 km (i.e., $t = 3.704 \text{ days}$) = 6.056 mg/L

and DO deficit at 100 km (i.e., $t = 4.63 \text{ days}$) = 5.427 mg/L

The DO deficit at different points along length of river is as below:

Distance in km	Time in days	DO deficit, mg/L	DO, mg/L
0	0	1.91	6.66
20	0.926	4.97	3.6
40	1.852	6.211	2.359
55.23	2.557	6.432	2.138
80	3.704	6.056	2.514
100	4.63	5.427	3.143



Republic of Iraq
Ministry of Higher Education and Scientific Research
University of Anbar
College of Engineering
Dams And Water Resources Department

Third Class

Water Quality Control

By

Professor : Majeed M. Ramal

Lecture : 9 - 1

DO, BOD, DO Sag Curve

Dissolved oxygen (DO)

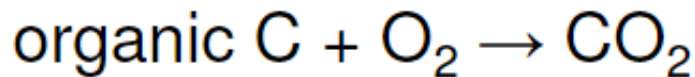
- What are factors that affect the amount of dissolved oxygen concentration in a river?
- What is the approximate dissolved oxygen concentration in a healthy natural water body?
- Which are the steps in developing a DO sag curve?
- How is the lowest DO concentration point in the sag curve called?
- If there was no change in the waste addition in a stream throughout the year, will the DO be higher in winter or summer?

Oxygen Demanding Wastes- measurement/estimation

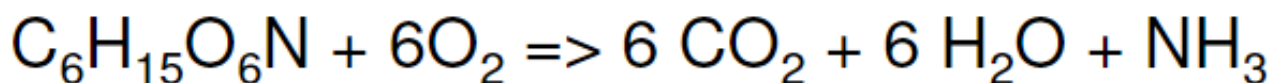
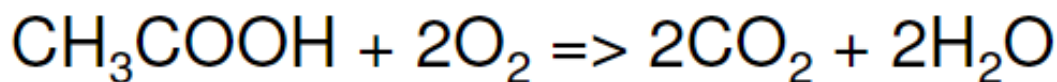
- Estimated stoichiometrically by theoretical oxygen demand (ThOD)
- Measured by oxygen demand potential
 - biochemical oxygen demand (BOD)
 - Nitrogenous oxygen demand (NBOD)
 - chemical oxygen demand (COD)

Oxygen-Demanding Wastes

- When organic substances are broken down in water, oxygen is consumed



- For example:



Oxygen-Demanding Wastes

- High oxygen levels necessary for healthy stream ecology.
- For example:
 - trout require 5-8 mg/L dissolved oxygen (DO)
 - carp require 3 mg/L DO

Effect of Oxygen Demanding Wastes on Rivers

- Amount of **dissolved oxygen (DO)** in water is the most commonly used indicator of a river's health.
- The solubility of oxygen depends on temperature, pressure, and salinity and the dissolved oxygen concentration in a healthy stream ranges from **7-9 mg/L**.
- As DO drops below **4 or 5 mg/L** the forms of life that can survive begin to be reduced.
- In an extreme case, when anaerobic conditions exist, most higher forms of life are killed.

Factors Affecting Amount of DO Available in Rivers

- **Oxygen demanding wastes** affect available DO
- **Tributaries** bring their own oxygen supply
- **Photosynthesis** adds DO during the day but the same plants remove oxygen at night
- **Respiration** of organisms living in water as well as in sediments remove oxygen
- In the summer rising temperatures reduce solubility of oxygen
- In the winter oxygen solubility increases, but ice may form blocking access to new atmospheric oxygen

Values of saturated dissolved oxygen, DO_s , as function of ambient temperature

Temperature (°C)	Oxygen (mg/L)	Temperature (°C)	Oxygen (mg/L)
0	14.6	13	10.6
1	14.2	14	10.4
2	13.8	15	10.2
3	13.5	16	10.0
4	13.1	17	9.7
5	12.8	18	9.5
6	12.5	19	9.4
7	12.2	20	9.2
8	11.9	21	9.0
9	11.6	22	8.8
10	11.3	23	8.7
11	11.1	24	8.5
12	10.8	25	8.4

U.S. EPA recommendation for a healthy fish population: $DO \geq 5$ mg/L.

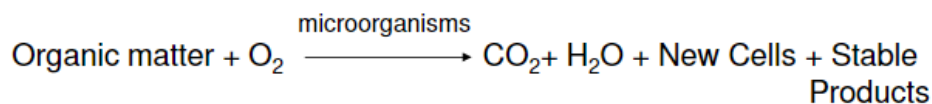
For the better fish, such as trout and salmon: $DO \geq 8$ mg/L.

$DO_s = f(\text{Temperature})$

When Temperature increase DO is Decreased

BOD

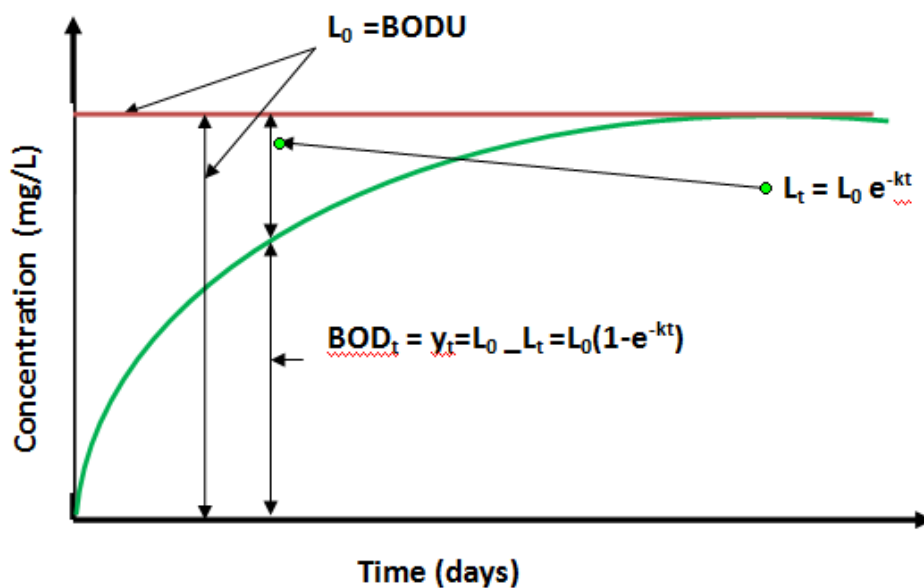
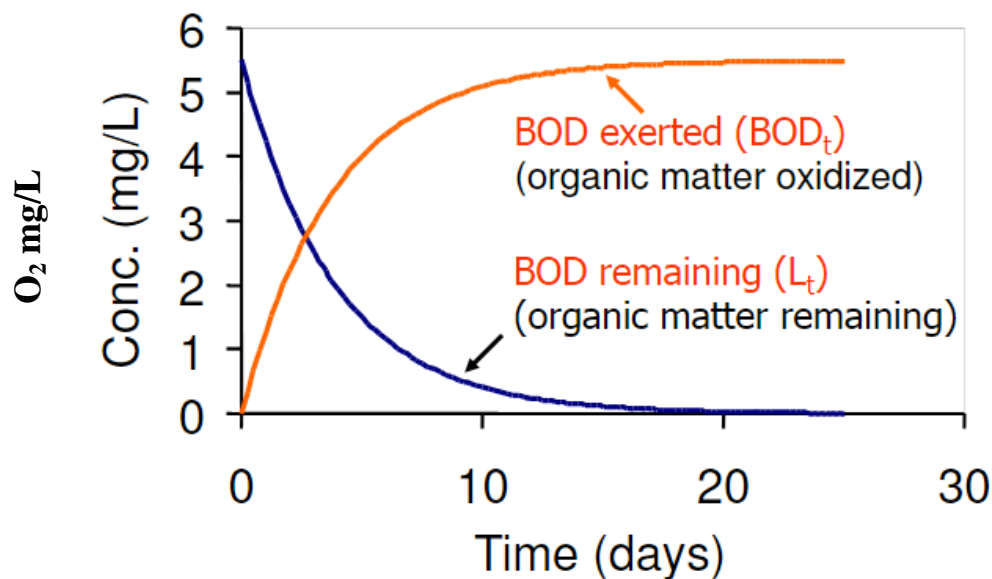
The amount of oxygen required by microorganisms to oxidize organic wastes aerobically is called biochemical oxygen demand (BOD)



$CBOD_5$ = The amount of O_2 exerted through five days

BOD

- It is expressed in mg of oxygen required per liter of wastewater (mg/L)
- The five-day BOD (BOD_5) is the total amount of oxygen consumed by microorganisms during the first five days of biodegradation



BOD for any time period can be determined as:

- The rate at which organics are utilized by microorganisms is assumed to be **a first-order reaction**,
- The rate at which organics utilized is proportional to the amount available.

$$\frac{dL_t}{dt} = -k \cdot L_t$$

where:

- L_t is the oxygen equivalent of the organics at time t (mg/L),
- k is the reaction constant (d^{-1})

$$\int_{L_0}^L \frac{dL_t}{L_t} = -k \int_0^t dt \Rightarrow \ln \frac{L_t}{L_0} = -kt \Rightarrow L_t = L_0 e^{-kt}$$

- L_0 is the total oxygen equivalent of the organics at time 0 (mg/L),
- L_t is the oxygen remaining at time t (mg/L),

The amount of oxygen used in the consumption of organics = **BOD**, can be found from the L_t value as the following:

If

- L_0 is the total oxygen equivalent of the total mass organics at time 0 (mg/L),
- L_t is the oxygen remaining at time t (mg/L),

$$Y_t = L_0 - L_t = L_0 - L_0 e^{-kt} \Rightarrow Y_t = L_0 (1 - e^{-kt})$$

Y_t represents the **BOD_t** of the water

Note:

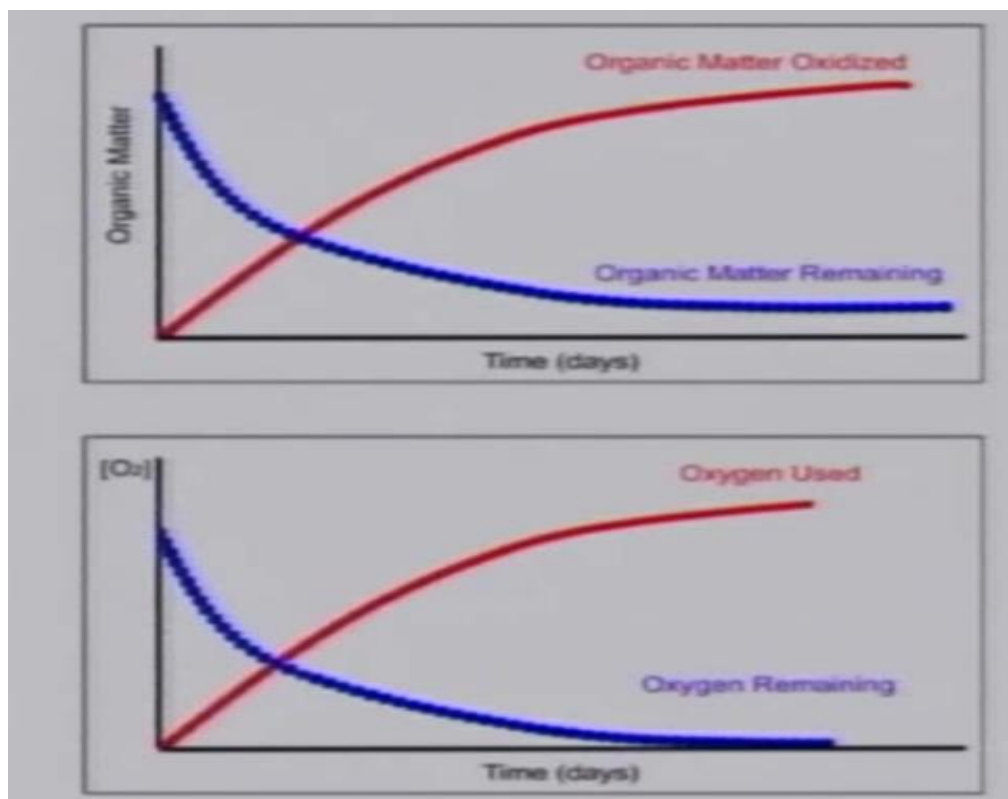
BOD (ultimate) = the initial oxygen equivalent of the water L_0

At any time, $L_0 = BOD_t + L_t$ (ultimate BOD equals the amount of DO demand used up and the amount of DO that could be used up eventually)

$$BOD_t = L_0 - L_t$$

- Replace L_t using: $L_t = L_0 e^{-kt}$
- To give: $BOD_t = L_0 - L_0 e^{-kt}$

- Simplified to: $\rightarrow BOD_t = L_0(1 - e^{-kt})$



Notes

- The water body is considered to be very clean if its BOD_5 at 20°C is less than 1 mg/litre (i.e. ppm).
- The water body is considered poor if its BOD_5 at 20°C is more than 5 mg/litre.
- The BOD_5 estimate however excludes complex organics such as cellulose, and proteins, which cannot be readily biodegraded by bacteria.

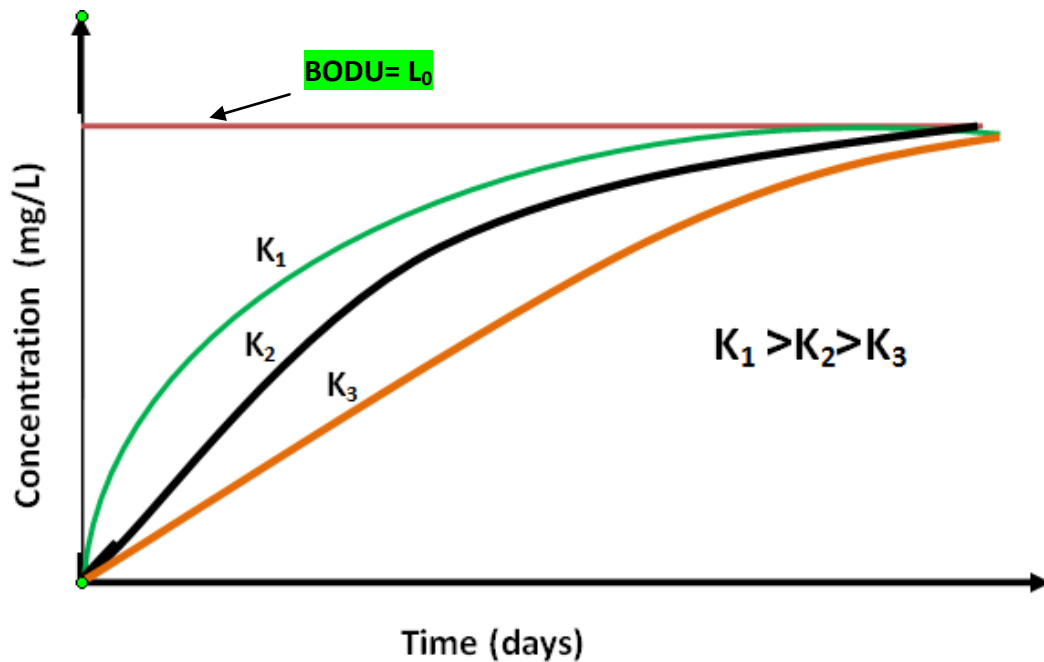
Reaction constant rate:

The de-oxygenation (Reaction) constant K , is obtained by laboratory test or field tests, and varies with temperature as given below:

$$K_T = K_{20}(\theta)^{T-20}$$

Where, $\theta = 1.047$

$K = 0.1$ to 0.3 for municipal sewage, base 10, (0.23 to 0.70 for base e)



Example:

The (BOD_5) of a wastewater @ $20^\circ C$) is (150 mg/L) , The (K) reaction constant rate is (0.23 per day- (d^{-1}) @ $20^\circ C$) , What would be the BOD_8 if the test were run at ($15^\circ C$) ?

Solution:

$$BOD_t = L_0(1 - e^{-kt})$$

$$BOD_u = L_0 = [BOD_5 / (1 - e^{-kt})]$$

$$BOD_u = L_0 = 150 / (1 - e^{-(0.23 \times 5)}) = 220 \text{ mg/L}$$

$$K_T = K_{20}(\theta)^{T-20}$$

$$K_{15} = 0.23(1.047)^{15-20} = 0.18 \text{ d}^{-1}$$

$$BOD_8 @ 15^\circ C = 220(1 - e^{-0.18 \times 8}) = 168 \text{ mg/L}$$

Iraq Republic of
Ministry of Higher Education and Scientific Research
University of Anbar
College of Engineering
Dams And Water Resources Department

Third Class

Water Quality Control

By

Professor : Majeed M. Ramal

Lecture – 10

Life of a Reservoir

Life of a Reservoir

The dead storage provided in reservoir capacity is allowed for sedimentation. Actually all the sediment load *does* not go in dead storage. It encroaches upon live storage also. The encroachment and its distribution depend upon many factors such as reservoir operation, valley characteristics, capacity inflow ratio, sediment content in the inflow etc. The useful life of a reservoir is taken till its capacity is reduced to about 20% of the designed capacity.

The rate of sedimentation is higher in the initial stages and it decreases with years. This is due to fall in the trap efficiency of the reservoir, consolidation and shrinkage of deposits and formation of delta.

Trap efficiency : The trap efficiency (η_t) is defined as the percent of the total inflow sediment which is retained in the reservoir. Thus

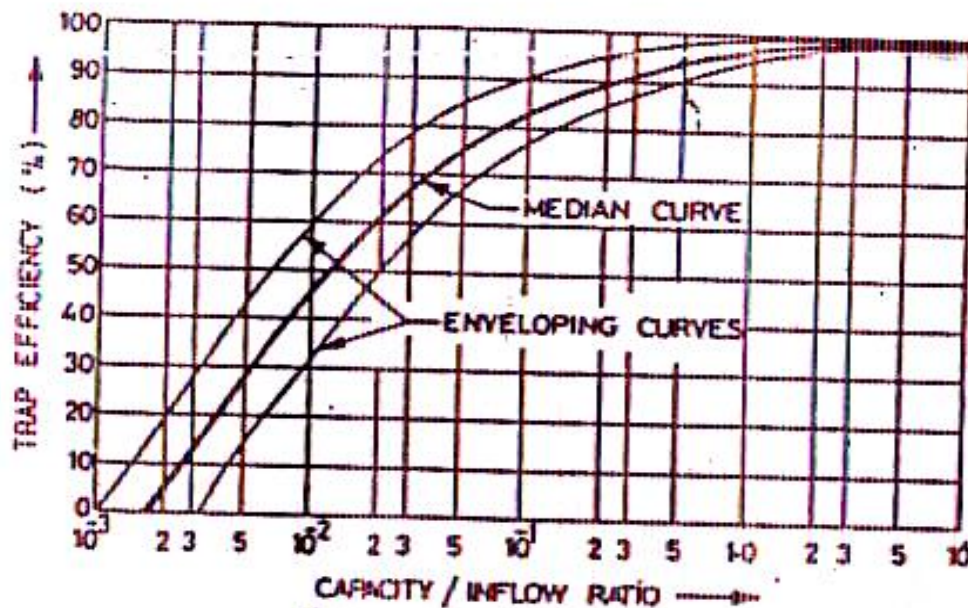
Trap efficiency

$$\eta_t = \left(\frac{\text{Sediment retained}}{\text{Total sediments}} \right) \times 100$$

(8)

From the observations of the rate of sedimentation is of existing reservoirs, it has been found that the trap efficiency of a reservoir depends upon the capacity/inflow ratio. Thus $\eta_t = f(\text{capacity/inflow ratio})$

Brune (1948) gave the curves relating the trap efficiency and the capacity/inflow ratio on the basis of sedimentation data of existing reservoirs (Fig. 14)



(Fig. 14)

The following procedure is used to estimate the useful life of reservoir. It is assumed that the capacity, the annual inflow, the annual sediment load, the trap efficiency and the mass density of the deposited sediments are known.

1. Determine the capacity – inflow ratio from the annual inflow volume and initial capacity of the reservoir.
2. Find the trap efficiency from Fig. 14 for the capacity – inflow ratio found in step(1).
3. Divide the available storage in different portions. Generally, it is divided into 10 portions. Compute the capacity – inflow ratio when the capacity is reduced to 90% of the initial capacity.
4. Determine the trap efficiency for the capacity – inflow ratio found in step (3).
5. Find the average of the trap efficiencies found in steps (2) and (4). This is the trap efficiency with the sedimentation takes place when capacity is reduced by first 10%(in this case).

6. Multiply the average annual sediment load by the average trap efficiency to determine the amount of sediment deposited annually.
7. Convert the deposited sediment from mass (or weight) units to the volume units by dividing the mass (or weight) of the sediment by the mass density (or specific weight).
8. Determine the number of years required for filling the 10% capacity of the reservoir by dividing this 10% capacity by the annual volume of sediment found in step (10).
9. Repeat the above steps and find out the number of years required for filling the successive 10% of the capacity till only 20% of the capacity is left, i.e. 80% of its is silted.
10. Calculate the sum of the number of years required for filling the successive 10% of the capacity. This sum total is equal to the useful life of the reservoir.

Example 4 : A reservoir has a capacity of 3.6 Mha-m up to the level of the spillway crest. The average annual inflow is 1.5 Mha-m of water. If the average annual sediment inflow 3×10^{11} kg. Determine the following:

- a. The useful life of the reservoir, assuming that usefulness of the reservoir is terminated which two – thirds of the total capacity is filled with sediment.
- b. The storage capacity at the end of 30 years.
- c. The period in which the reservoir will be completely filled up to the crest level.

Assume mass density of sediments as 1100 kg/m^3 .

Consider only 6 divisions of the total storage capacity.

Solution Annual sediment inflow = $3 \times 10^{11} \text{ kg}$.

$$= \frac{3 \times 10^{11}}{1100} \text{ m}^3 = 272.73 \text{ Mm}^3 = 0.0273 \text{ Mha-m}$$

$$\text{Annual inflow of water} = 1.5 \text{ Mha-m}$$

$$\text{Initial capacity – inflow ratio} = \frac{3.6}{1.5} = 2.4$$

$$\text{Storage capacity at the end of useful life} = 1/3 \times 3.6 = 1.2 \text{ Mha-m}$$

$$\text{Capacity – inflow ratio} = \frac{1.2}{1.5} = 0.8$$

$$\text{Volume of sediment deposited in 30 years} = 30 \times 0.0273 = 0.82 \text{ Mha-m}$$

$$\text{Storage capacity at the end of 30 years} = 3.6 - 0.82 = 2.78 \text{ Mha-m}$$

$$\text{Capacity – inflow ratio} = \frac{2.78}{1.5} = 1.85$$

When the reservoir is completely filled with the sediment, Capacity – inflow ratio = 0.0

The calculations are shown in the table below. The values of the trap efficiency are obtained from

S. No.	Capacity (Mha-m)	Capacity inflow ratio	Trap efficiency		Annual trapped sediment		Incremental volume Mha-m	No. of years required
			Point efficiency (100%)	Average efficiency (100%)	Mass (kg)	Volume (Mha-m)		
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	3.60	2.40	98.2					
2	3.00	2.00	98.0	98.1	2.943×10^{11}	0.0268	0.60	22.4
3	2.40	1.60	97.5	97.75	2.933×10^{11}	0.0266	0.60	22.6
4	1.80	1.20	97.0	97.25	2.918×10^{11}	0.0265	0.60	22.7
5	1.20	0.80	96.0	96.5	2.895×10^{11}	0.0263	0.60	22.8
6	0.60	0.40	95.0	95.5	2.865×10^{11}	0.0260	0.60	23.1
7	0	0	0	47.5	1.425×10^{11}	0.0130	0.60	46.2

159.8 years

$$\text{Useful life of reservoir} = 22.4 + 22.6 + 22.7 + 22.8 = 90.5 \text{ years}$$

$$\text{Storage Capacity at the end of 30 years} = 2.78 \text{ Mha – m}$$

$$\text{Total life of reservoir} = 159.8 \text{ years.}$$