

الكيمياء

معالجة المياه

سنتر فيوتشر



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Subject:..... كيمياء «اعبادى»

Chapter:..... معالجة المياه

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* Hardness of water

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هي قدرة الماء على استهلاك الصابون وتكوين رغوة
يسمى بـ عسر الماء

is measure of its capacity to precipitate soap due to the presence of divalent cations of Ca^{+2} & Mg^{+2}

$$\text{Total hardness (TH)} = \text{Ca}^{+2} \text{ hardness} + \text{Mg}^{+2} \text{ hardness}$$

* Calculation of Ca^{+2} hardness (mg/L as CaCO_3)

$$\frac{\text{Ca}^{+2} \text{ hardness (mg/L as CaCO}_3\text{)}}{\text{eq. wt of CaCO}_3} = \frac{\text{Calcium (mg/L)}}{\text{eq. wt of Calcium}}$$

الوزن الجزيئي as equivalent weight = $\frac{\text{Molecular weight}}{\text{Valence}}$ التكافؤ

$$\therefore \frac{\text{Ca}^{+2} \text{ hardness (mg/L as CaCO}_3\text{)}}{50.04} = \frac{\text{Calcium (mg/L)}}{20.04} \quad \text{Ca} \rightarrow 40$$

* Calculation of Mg^{+2} hardness (mg/L as CaCO_3)

$$\frac{\text{Mg}^{+2} \text{ hardness (mg/L as CaCO}_3\text{)}}{\text{eq. wt of CaCO}_3} = \frac{\text{Magnesium (mg/L)}}{\text{eq. wt of magnesium}}$$

$$\frac{\text{Mg}^{+2} \text{ hardness (mg/L as CaCO}_3\text{)}}{50.04} = \frac{\text{Magnesium (mg/L)}}{12.15} \quad \text{Mg} \rightarrow 24$$

$$\therefore \text{Total hardness} = \text{Ca}^{+2} \text{ hardness} + \text{Mg}^{+2} \text{ hardness}$$

$$\text{mg/L as CaCO}_3 = \text{mg/L as CaCO}_3 + \text{mg/L as CaCO}_3$$

Example:-

A sample of water has Calcium content of 70 mg/L as CaCO_3 and magnesium content of 90 mg/L as CaCO_3

$$\therefore \text{Total hardness} = 70 + 90 = 160 \text{ mg/L as CaCO}_3$$

* Hardness of Water

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* Calculation of Mg^{+2} hardness (mg/L as CaCO_3)

$$\frac{\text{Mg}^{+2} \text{ hardness (mg/L as CaCO}_3\text{)}}{\text{eq. wt of CaCO}_3} = \frac{\text{Magnesium (mg/L)}}{\text{eq. wt of magnesium}}$$

$$\frac{\text{Mg}^{+2} \text{ hardness (mg/L as CaCO}_3\text{)}}{50.04} = \frac{\text{Magnesium (mg/L)}}{12.15} \quad \text{Mg} \rightarrow 24$$

$$\therefore \text{Total hardness} = \text{Ca}^{+2} \text{ hardness} + \text{Mg}^{+2} \text{ hardness}$$

$$\text{mg/L as CaCO}_3 = \text{mg/L as CaCO}_3 + \text{mg/L as CaCO}_3$$

Example:-

A sample of water has Calcium content of 70 mg/L as CaCO_3 and magnesium content of 90 mg/L as CaCO_3

$$\therefore \text{Total hardness} = 70 + 90 = 160 \text{ mg/L as CaCO}_3$$

Example 1

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Determine the total hardness as CaCO_3 of sample of water that has Calcium Content of 28 mg/L and magnesium Content of 9 mg/L

Solution

$$\frac{\text{Calcium hardness (mg/L as CaCO}_3\text{)}}{\text{eq. wt of CaCO}_3} = \frac{\text{calcium (mg/L)}}{\text{eq. wt of Calcium}}$$

$$\frac{X}{50.04} = \frac{28 \text{ mg/L}}{20.04}$$

$$X = 69.9 \text{ mg/L as CaCO}_3$$

$$\frac{\text{Magnesium hardness (mg/L as CaCO}_3\text{)}}{\text{eq. wt of CaCO}_3} = \frac{\text{Magnesium (mg/L)}}{\text{eq. wt of magnesium}}$$

$$\frac{Y}{50.04} = \frac{9 \text{ mg/L}}{12.15}$$

$$X = 37.1 \text{ mg/L as CaCO}_3$$

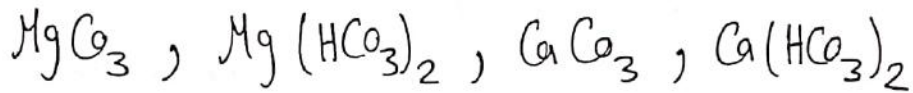
$$\begin{aligned} \text{Total hardness} &= \text{Ca}^{+2} \text{ hardness} + \text{Mg}^{+2} \text{ hardness} \\ \text{mg/L as CaCO}_3 &= \text{mg/L as CaCO}_3 + \text{mg/L as CaCO}_3 \end{aligned}$$

$$\therefore \text{Total hardness} = 69.9 + 37.1 = 107 \text{ mg/L as CaCO}_3$$

* Carbonate Hardness (CH) %

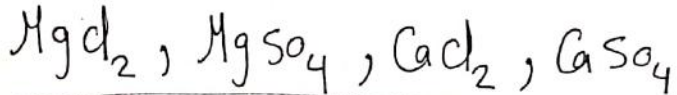
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Carbonate hardness caused by bicarbonate salts of Ca^{+2} & Mg^{+2} also Ca^{+2} & Mg^{+2} combined with carbonate



* Non-Carbonate Hardness (NCH) %

Calcium and magnesium salts other than carbonate and bicarbonate salts



$$\text{Total hardness} = \text{Carbonate hardness} + \text{Non-Carbonate hardness}$$

→ If Alkalinity < T.H

$$\therefore \text{Alkalinity} = \text{Carbonate hardness}$$

$$\therefore \text{Total hardness} = \text{Alkalinity} + \text{Non-Carbonate hardness}$$

→ If Alkalinity \geq T.H

$$\therefore \text{T.H} = \text{Carbonate hardness}$$

$$\therefore \text{Non-Carbonate hardness} = \text{Zero}$$

Example | A sample of water has 210 mg/L Alkalinity and 330 mg/L total hardness, Find out Carbonate and non-Carbonate Hardness

$$\text{T.H} > \text{Alkalinity}$$

$$\therefore \text{Carbonate hardness} = \text{Alkalinity} = 210 \text{ mg/L}$$

$$\text{Non-Carbonate Hardness} = \text{T.H} - \text{Carbonate hardness}$$

$$= 330 - 210 = 120 \text{ mg/L}$$

(*) Types of Hardness :-
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(1- temporary Hardness) called Carbonate hardness

Caused by Ca^{+2} & Mg^{+2} Carbonates and bicarbonate

removed by - Boiling
- Addition of lime

(2- Permanent Hardness) called non-Carbonate hardness

Caused by sulphates, chlorides and Nitrates of Ca^{+2} & Mg^{+2}

removed by - Lime-soda process
- Ion exchange or Zeolite
- Demineralization
- Reverse Osmosis

(Water softening) mean Removal of Hardness إزالة عسر الماء

There're 3 Basic ways to soften water :-

- 1- Remove of Ca^{+2} & Mg^{+2} ions from water إزالة الأيونات المسببة لعسر الماء
- 2- Force insoluble substance (such as CaCO_3 , $\text{Mg}(\text{OH})_2$) to precipitate before enter the system إجبار الأيونات الغير ذائبة على الترسيب
- 3- prevent Ca^{+2} ions to forming CaCO_3 by Complexing them تفاعل Ca^{+2} مع مادة أخرى وتكوين Complex ومنع Carbonate ذائبة في الماء

Example] A water sample contains 110 mg/L alkalinity as CaCO_3

and 105 mg/L total hardness as CaCO_3

What is the Carbonate and non-Carbonate hardness of sample??

Solution

\therefore Alkalinity $>$ total hardness

\therefore T.H = Carbonate hardness = 105 mg/L as CaCO_3

& Non-Carbonate hardness = Zero

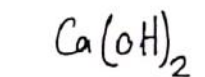
* Hardness Range

Hardness Concentration mg/L	Degree of Hardness
0 - 60	Soft
60 - 120 ← مقبولة	Moderately Hard
120 - 180	Hard
180 and over < سوف يتم المعالجة	Very Hard

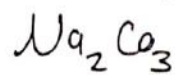
* Problems Caused by Hardness %

- 1- Excessive soap is needed for washing استهلاك كميات كبيرة من الصابون
as detergents work less efficiently because anions (surfactant المستولدة عن)
which meant to hold dirt particles will react with Ca^{+2} & Mg^{+2}
- 2- Soap based on animal fats will react with Ca^{+2} & Mg^{+2} forming ppt on skin and clothes
- 3- Some food become tough when cooked in hard water
as Ca^{+2} ions cause cross-linking between molecules of food and prevent water entering, food remain hard
- 4- Scale clog سد pipes and fittings تقلل من كفاءة المعدات
and become 90% less efficient

→ Lime Softening % chemicals used Lime & Soda Ash



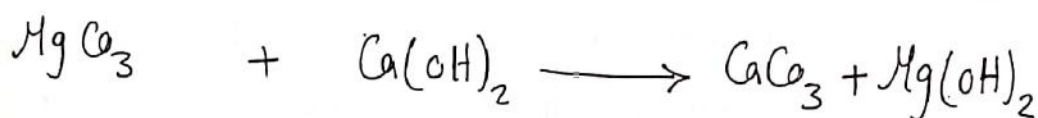
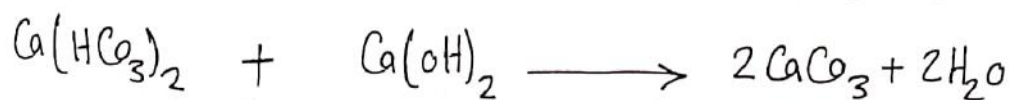
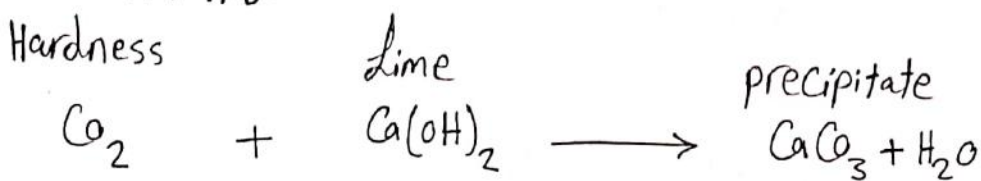
↓
to remove
Carbonate
hardness



↓
to remove
non-Carbonate
hardness

→ Lime Addition %

Hardness



⇒ Quick Lime dosage can be calculated with formula:-

$$\text{Quick Lime mg/l as CaO} = \frac{(A+B+C+D) \times (\text{Excess \%} + 1)}{\text{purity of lime}}$$

A → Carbon Dioxide in source water
mg/l $\text{CO}_2 \times 1.27$

B → Bicarbonate Alkalinity
mg/l $\text{CaCO}_3 \times 0.56$

C → Hydroxide Alkalinity
mg/l $\text{CaCO}_3 \times 0.56$

D → Magnesium removed in softening
mg/l as $\text{Mg}^{+2} \times 2.30$

www.CollegeTanta.gov Soda Ash dosage can be calculated with formula :-

$$\text{Soda Ash mg/L as Na}_2\text{CO}_3 = \frac{X * (\text{Excess \%} + 1)}{\text{purity of soda}}$$

$$X \text{ Soda Ash mg/L as Na}_2\text{CO}_3 = \frac{\text{non carbonate hardness mg/L as CaCO}_3}{100} \times 106$$

$$" = " \times 1.06$$

$$\text{non-carbonate hardness mg/L as CaCO}_3 \rightarrow \text{non-carbonate hardness mg/L as Na}_2\text{CO}_3$$

$$\text{M.Wt of CaCO}_3 \rightarrow \text{M.Wt of Na}_2\text{CO}_3$$

Example The following test results were provided by laboratory

CO₂ Concentration 25 mg/L as CO₂

HCO₃ bicarbonate Conc 205 mg/L as CaCO₃

Mg magnesium Conc 9 mg/L as Mg

non-carbonate hardness Concentration 95 mg/L as CaCO₃

Assuming no excess lime is added, Find correct dosage for lime (Containing 90% pure CaO) and soda Ash (Containing 99% pure Na₂CO₃) required to remove all hardness

Solution

$$\text{CO}_2 \rightarrow A = 25 \text{ mg/L} \times 1.27 = 31.75 \text{ mg/L as CaO}$$

$$\text{HCO}_3 \rightarrow B = 205 \text{ mg/L} \times 0.56 = 114.8 \text{ mg/L as CaO}$$

$$\text{Mg} \rightarrow D = 9 \text{ mg/L} \times 2.30 = 20.79 \text{ mg/L as CaO}$$

$$\therefore \text{Quick lime dosage mg/L as CaO} = \frac{(31.75 + 114.8 + 20.79) \times 1}{0.9} = 185.9 \text{ mg/L as CaO}$$

$\Sigma = 95 \text{ mg/L} \times 1.06 = 100.7 \text{ mg/L as } \text{Na}_2\text{CO}_3$

Soda Ash dosage
 $\text{mg/L as } \text{Na}_2\text{CO}_3 = \frac{100.7 \times 1}{0.99} = 101.7 \text{ mg/L as } \text{Na}_2\text{CO}_3$

Example 1

A water sample has Carbon dioxide content of 4 mg/L as CO_2 , total Alkalinity of 130 mg/L as CaCO_3 and magnesium content of 26 mg/L as Mg^{+2} , How much quick lime will be required for softening? if purity of lime is 90% and use 15% excess of lime

Solution

$\text{CO}_2 \rightarrow A = 4 \text{ mg/L} \times 1.27 = 5 \text{ mg/L as CaO}$

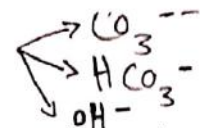
Alkalinity $\rightarrow B = 130 \text{ mg/L} \times 0.56 = 73 \text{ mg/L as CaO}$

$C = \text{Zero}$

Magnesium $\rightarrow D = 26 \text{ mg/L} \times 2.30 = 60 \text{ mg/L as CaO}$

$\therefore \text{Quick lime dosage}$
 $\text{mg/L as CaO} = \frac{(A+B+C+D) \times \text{Excess \%}}{\text{purity of lime}}$

" $= \frac{(5 + 73 + 60 \text{ mg/L}) \times 1.15}{0.9} = 176 \text{ mg/L as CaO}$



- the alkalinity of water is primarily due to carbonate, bicarbonate and hydroxide content

- Alkalinity measure the acid-neutralizing capacity of water

كمية الحمض المستهلك لتعادل كافي Alkalinity

- Higher alkalinity, the greater capacity of water to neutralize acids

phenolphthalein Alkalinity
at pH=8.3 mg/L as $\text{CaCO}_3 = \frac{A \times N \times 50,000}{\text{ml of sample}}$

Total Alkalinity
at pH=4.5 mg/L as $\text{CaCO}_3 = \frac{B \times N \times 50,000}{\text{ml of sample}}$

where, A → titrant used to pH=8.3

B → titrant used to pH=4.5

N → Normality of Acid (Ex:- 0.02 N H_2SO_4)

50,000 → factor

(*) Determination Bicarbonate, Carbonate and hydroxide Alkalinity %

	Bicarbonate Alkalinity	Carbonate Alkalinity	Hydroxide Alkalinity
① $P=0$	T	0	0
② $P < \frac{1}{2}T$	$T - 2P$	$2P$	0
③ $P = \frac{1}{2}T$	0	$2P$	0
④ $P > \frac{1}{2}T$	0	$2T - 2P$	$2P - T$
⑤ $P = T$	0	0	T

Example 1 Results of Alkalinity titrations on water sample as follow: — Sample was 100 ml

- 1.4 ml titrant was used to pH 8.3
- 2.4 ml titrant was used to pH 4.5
- Acid normality was 0.02 N H_2SO_4

What is phenolphthalein, total Alkalinity ??

BiCarbonate, Carbonate and hydroxide Alkalinity ??

Solution

$$\begin{aligned}\text{Ph. ph Alkalinity} \\ (\text{mg/L as } CaCO_3) &= \frac{1.4 \text{ ml} \times 0.02 \text{ N} \times 50,000}{100 \text{ ml}} \\ &= 14 \text{ mg/L as } CaCO_3\end{aligned}$$

$$\begin{aligned}\text{Total Alkalinity} \\ (\text{mg/L as } CaCO_3) &= \frac{2.4 \text{ ml} \times 0.02 \text{ N} \times 50,000}{100 \text{ ml}} \\ &= 24 \text{ mg/L as } CaCO_3\end{aligned}$$

From table $P > \frac{1}{2}T$

\therefore BiCarbonate Alkalinity = Zero

Carbonate Alkalinity = $2T - 2P$

$$= 2(24) - 2(14) = 20 \text{ mg/L as } CaCO_3$$

Hydroxide Alkalinity = $2P - T$

$$= 2(14) - 24 = 4 \text{ mg/L as } CaCO_3$$

