Course Number : CE 332
Course Name : Environmental Engineering Lab
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Experiment No. 6
Determination of Alkalinity of Water

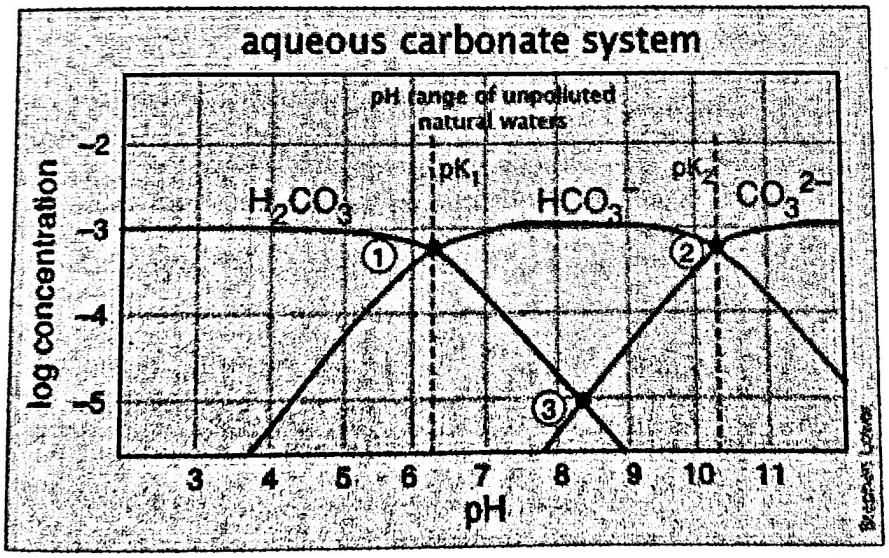
INTRODUCTION

The ***alkalinity*** of water is a measure of its capacity to neutralize acids. The term ***acid neutralizing capacity*** **(ANC)** is sometimes used. The alkalinity of natural waters is due primarily to the salts of weak acids, although weak or strong bases may also contribute. Bicarbonates represent the major form of alkalinity, since they are formed in considerable amounts from the action of carbon dioxide upon basic materials in the soil (as shown in Eq.1).

$$CO_2 + CaCO_3 + H_2O = Ca^{2+} + 2\,HCO_3^- \qquad (1)$$

Other salts of weak acids, such as borates, silicates, and phosphates, may be present in small amounts. A few organic acids, for example humic acid, form salts that add to the alkalinity of natural waters.

Although many materials may contribute to the alkalinity of water, the major portion of the alkalinity in natural waters is caused by three major types of chemical constituents: (i) hydroxide, (ii) carbonate, and (iii) bicarbonate. For most practical purposes, alkalinity due to other materials in natural waters is insignificant and may be ignored. The predominance of different carbonate species (closed syatem) is shown in Fig 1.



$pK_1 = 6.37$
$pK_2 = 10.33$

Figure 1: Logarithmic concentration diagram for 0.001 M Carbonic Acid (Source: Sawyer et al., 1994)

ENVIRONMENTAL SIGNIFICANCE

The alkalinity of waters is due principally to salts of weak acids and strong bases, and such substances act as buffer to resist a drop in pH resulting from acid additions. Alkalinity is thus a measure of the buffer capacity and in this sense is used to a great extent in wastewater treatment practice. Alkalinity is

very important in iron removal from water by oxidation-precipitation process. It has been found that rate of oxidation of dissolved ferrous iron (Fe^{2+}) into insoluble ferric iron is vary slow for low alkaline waters (alkalinity less than 130 mg/l as $CaCO_3$). Because the alkalinity of many waters is primarily a function of carbonate, bicarbonate and hydroxide content, it is taken as an indication of the concentration of these constituents. Alkalinity of water has little public health significance. Highly alkaline waters are usually unpalatable.

THEORY

Alkalinity is measured volumetrically by titration with *N/50* (i.e., 0.02 N) H_2SO_4 and is reported in terms of equivalent $CaCO_3$. For samples with initial pH is above 8.3, the titration is made in two steps. In the first step, the titration is conducted until the pH is lowered to 8.3, the point at which phenolphthalein indicator turns from pink to colorless. The second phase of the titration is conducted until the pH is lowered to about *4.5*, corresponding to the methyl orange (or bromocresol green) end point. When the pH of a sample is less than 8.3, a single titration is made to a pH of *4.5*. The first end point of pH 8.3 corresponds to the equivalence point for the conversion of carbonate to bicarbonate (Eq. 2, Fig 1). When alkalinity is measured to the phenolphthalein end point (pH 8.3), it is called phenolphthalein alkalinity which is due to the presence of either hydroxide or carbonate or both.

$$CO_3 + H^+ = HCO_3^- \qquad (2)$$

The pH of about 4.5 used as the end point for the second step of the titration corresponds approximately to the equivalence point for the conversion of bicarbonate ion to carbonic acid (Eq. 3, Fig 1). When alkalinity is measured to the methyl orange (or bromocresol green) end point, it is called methyl orange alkalinity or total alkalinity which is due to the presence of hydroxide, carbonate, and bicarbonate.

$$HCO_3^- + H^+ = CO_3^{2-} \qquad (3)$$

REAGENTS

1. Phenolphthalein indicator
2. Standard 0.02N (or N/50) sulfuric acid
3. Methyl orange indicator

APPARATUS

1.Beaker	:2 pc
2. Measuring cylinder	:lpc
3. Dropper	:lpc
4. Stirrer	:lpc

PROCEDURE

(I) Take 100 ml. of the sample into one beaker and the same amount of distilled water into another beaker.

(2) Measure pH of the sample with a pH meter.

(3) Add 3 drops of phenolphthalein indicator to each. If the sample becomes pink, go to step (3). Otherwise, go to step (4).

(4) Add 0.02N H_2SO_4 acid from a burette until the pink color just disappears. Record the ml. of the acid used.

(5) Add 3 drops of methyl orange indicator to each beaker. If the sample becomes yellow add 0.02N H_2SO_4 acid until the first change in color is noted. The end point is a slight orange tinge. Record the ml. of acid used.

CALCULATION

Thus, Phenolphthalein Alkalinity = (ml of N/50 H_2SO_4 to pH 8.3) × 1000 / (ml of sample)

= (ml of H_2SO_4 to pH 8.3) × Multiplying Factor (MF) (4)

and, Total Alkalinity = (total ml of N/50 H_2SO_4 to pH approx. 4.5) × 1000 / (ml of sample)
= (total ml of H_2SO_4 to pH approx. 4.5) × Multiplying Factor (MF) (5)

where, MF = normality of H_2SO_4 × equivalent wt. of $CaCO_3$ × 1000/ (ml of sample taken)

HYDROXIDE, CARBONATE, AND BICARBONATE ALKALINITY

In water analysis it is often desirable to know the kinds and amounts of the various forms of alkalinity present. This information is especially needed in water-softening processes and in boiler-water analysis.

There are three procedures commonly used to make these calculations:
(1) Calculation from alkalinity measurements alone,
(2) Calculation from alkalinity plus pH measurements, and
(3) Calculation from equilibrium equations.

The first is the classical method and is based on empirical relationships for the calculation of the various forms of alkalinity from phenolphthalein and total alkalinities. This is intended for use by technicians and others who do not have knowledge on the fundamental chemistry involved.

The second procedure gives sufficiently accurate estimates for most practical purposes, and also makes use of phenolphthalein and total alkalinity measurements. In addition, an accurate initial pH measurement is required for the direct calculation of hydroxide alkalinity.

In the third procedure, the various equilibrium equations for carbonic acid are used to compute the concentrations of the various alkalinity forms. This method gives reasonably accurate results for constituents, even when present in fractional mg/l range. A total alkalinity, as well as a pH measurement, is required. In addition, a dissolved solid measurement to correct for 'ion activity and a temperature measurement for the selection of a proper equilibrium constant are needed. However, reasonably accurate results are obtained without these two data if the dissolved solids concentration is not too high and water temperature is around 25 ^{0}C. Description of all three procedures are available in Sawyer et al. (1994). The following section describes only the third procedure to determine hydroxide, carbonate and bicarbonate alkalinities.

Calculation from Equilibrium Equations
The relevant equilibrium equations are as follows:

$$H_2O = H^+ + OH^- \quad (6a)$$

$$K_W = \{H^+\}\{OH^-\} = 10^{-14} \text{ (at 25 °C)} \quad (6b)$$

$$H_2CO_3 = H^+ + HCO_3^- \quad (7a)$$

$$K_{A1} = \{H^+\}\{HCO_3^-\} / \{H_2CO_3\} = 10^{-6.3} \text{ (at 25 °C)} \quad (7b)$$

$$HCO_3^- = H^+ + CO_3^{2-} \quad (8a)$$

$$K_{A2} = \{H^+\}\{CO_3^{2-}\} / \{HCO_3^-\} = 10^{-10.3} \text{ (at 25 °C)} \quad (8b)$$

The alkalinity of water can be expressed as follows:

$$\text{Total alkalinity (mg/l as } CaCO_3) / 50{,}000 = (HCO_3^-) + 2\,(CO_3^{2-}) + (OH^+) - (H^+) \quad (9)$$

From the above equations, the following expressions for different alkalinities can be derived:

$$\text{Carbonate alkalinity (mg/l as } CaCO_3) = [50{,}000\ \{(\text{alkalinity}/50{,}000) + (H^+) - (K_w/(H^+)\}] / [1 + \{(H^+)/2K_{A2}\}] \quad (10)$$

$$\text{Bicarbonate alkalinity (mg/l as } CaCO_3) = [50{,}000\ \{(\text{alkalinity}/50{,}000) + (H^+) - (K_w/(H^+)\}] / [1 + \{2K_{A2}/(H^+)\}] \quad (11)$$

It should be noted that the equilibrium constants vary with temperature and activities of ions vary with concentration of ions in water. If temperature of water varies significantly from 25 ^oC and ionic strength of water is high (that is high concentration dissolved ions), appropriate corrections need to be incorporated in the above equations. Otherwise these equations would give reasonably accurate results. Sometimes actual concentrations of carbonate and bicarbonate ions may be desired. Conversions to mg/l of CO_3^{2-} and HCO_3^- are as follows:

$$\text{mg/l } CO_3^{2-} = \text{mg/l carbonate alkalinity} \times 0.6 \quad (12)$$

$$\text{mg/l } HCO_3^- = \text{mg/l bicarbonate alkalinity} \times 1.22 \quad (13)$$

Molar concentrations may be obtained as follows:

$$(CO_3^{2-}) = (\text{mg/l } CO_3^{2-}) / 60{,}000 \quad (14)$$

$$(HCO_3^-) = (\text{mg/l } HCO_3^-) / 61{,}000 \quad (15)$$

ASSIGNMENT QUESTIONS

(1) Discuss the environmental significance of alkalinity.

(2) Define total alkalinity, phenolphthalein alkalinity, and methyl orange alkalinity?

(3) Calculate hydroxide, bicarbonate, and carbonate alkalinities of a water sample with a total alkalinity of 250 mg/l as $CaCO_3$ and a pH of 7.8. Which type of alkalinity dominates the total alkalinity? Also calculate the concentrations of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions. [Hint: Use Eqs. 10-15]