Chapter 1

Introduction

Water from a natural resource is usually not sufficiently pure, thus it cannot be used for human consumption or in industries without appropriate treatments. Water must be treated before uses in order to make it suitable for each process or to prevent from harmful environment. In the former purpose, chlorine is usually added for disinfection.

1.1 Chlorination

Chlorination is one of the most common methods for the destruction of pathogenic and other harmful organisms that may endanger human health. Chlorination of water can remove bacteria up to 98-99 %.[1] Common chlorine compounds used in water treatment process are chlorine gas (Cl_2), calcium hypochlorite [$Ca(OCl)_2$], sodium hypochlorite ($NaOCl$) and chlorine dioxide (ClO_2). Hypochlorite reduces its available strength on storage vessel and may be difficult to handle. Because calcium hypochlorite tends to crystallize, it may clog metering pump, piping and valves. The handling of sodium hypochlorite requires special design because of its corrosiveness and the presence of chlorine fumes. Chlorine gas is very toxic and very corrosive. Chlorine dioxide can be generated by the reaction between sodium chlorite solution and chlorine. Because sodium chlorite is about ten times as expensive as chlorine on a weight basis, economical consideration must be
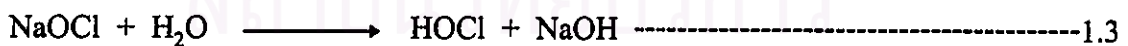
taken into account. Most water treatment process, however, use liquid chlorine instead.
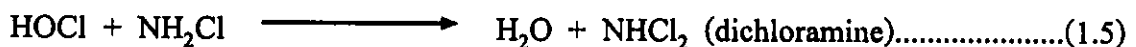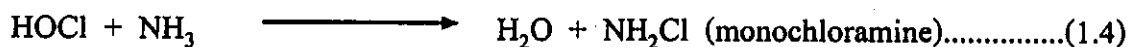
Chemistry of Chlorine

Chlorine, which is in gas phase at standard state, is heavier than air, greenish yellow-colored, toxic gas. It is a strong oxidizing agent reacting with most elements and compounds. Chlorine combines with water forming hypochlorous acid (HOCl) which, in turn, can ionize to the hypochlorite ion, OCl^-. Below pH 7, a small portion of the HOCl ionizes to OCl^-, while, above pH 8, the majority is in the form of OCl^- as chemical reaction below
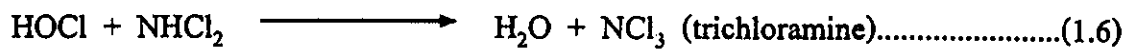
$$Cl_2 + H_2O \longrightarrow HCl + HOCl \underset{pH<7}{\overset{pH>8}{\rightleftharpoons}} H^+ + OCl^- \text{--------1.1}$$
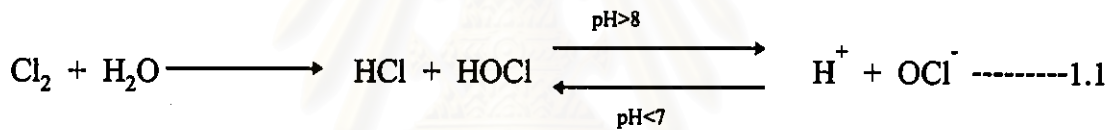
The HOCl and OCl^- in water is called "free available chlorine". The killing efficiency of HOCl is about 40 to 80 times that of OCL^-. Free chlorine can also be added into water in form of hypochlorite salts. The reactions are as follows:

$$Ca(OCl)_2 + 2H_2O \longrightarrow 2HOCl + Ca(OH)_2 \text{----------------------------1.2}$$
$$NaOCl + H_2O \longrightarrow HOCl + NaOH \text{--------------------------------------1.3}$$

Untreated water contains nitrogen in the form of ammonia and various combined organic forms. Chlorine readily reacts with ammonia in water to form chloramines as follows:

$$HOCl + NH_3 \longrightarrow H_2O + NH_2Cl \text{ (monochloramine)...............(1.4)}$$
$$HOCl + NH_2Cl \longrightarrow H_2O + NHCl_2 \text{ (dichloramine)....................(1.5)}$$

$$HOCl + NHCl_2 \longrightarrow H_2O + NCl_3 \text{ (trichloramine)}................(1.6)$$

The reaction products formed depend on pH, temperature, time, and initial chlorine to ammonia ratio. Monochloramine are formed in the pH range of 4.5 to 8.5. Above pH 8.5 monochloramine generally exists alone, but below pH 4.4 trichloramine is produced. Chlorine existing in chemical chlorination with ammonia nitrogen or organic nitrogen compounds is defined as combined available chlorine.

When chlorine is added into water containing ammonia, the residuals that develop yield a curve similar to that is shown in Figure 1.1
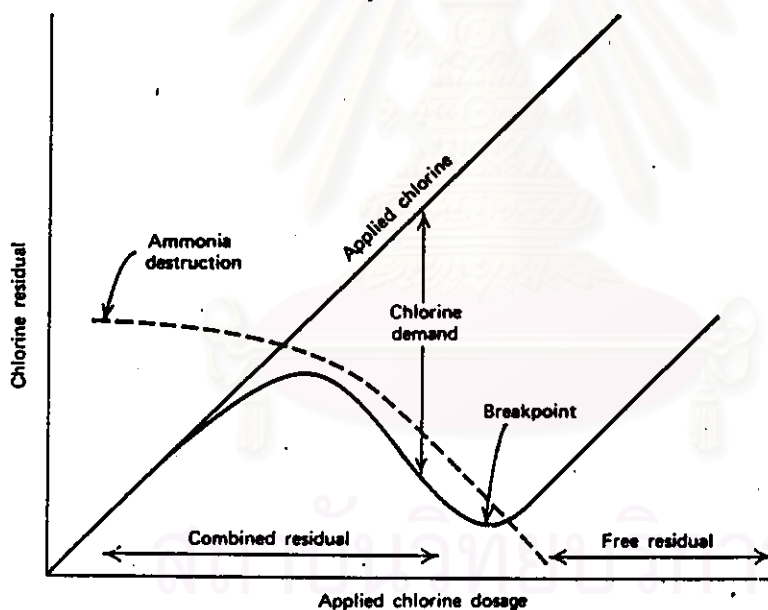

Figure 1.1. Typical breakpoint chlorination curve[2]

The straight line from the origin is the concentration of chlorine applied, or the residual chlorine if the applied chlorine is not consumed. The curved line represents chlorine residual, corresponding to various dosages, after a certain contact time, such as 20 min.

Chlorine reacts with ammonia in water to form chloramines. Chlorine residuals declines to a minimum value referred as the breakpoint. Dosage in excess of this breakpoint produces free chlorine residuals. Bactericide action of combined available chlorine is significantly less than that of free chlorine residuals. The main purpose of adding excess chlorine is to ensure sufficient disinfection for a certain period, for instance 3 day storage. Recommended minimum bactericidal chlorine residuals are listed in Table 1.1

Table 1.1 Recommended minimum bactericidal chlorine residuals for disinfection[2]

pH Value	Minimum Free Available Chlorine Residual After 10 Min Contact (mg/l)	Minimum Combined Available Chlorine Residual After 60 Min Contact (mg/l)
6.0	0.2	1.0
7.0	0.2	1,5
8.0	0.4	1.8
9.0	0.8	>3.0
10.0	0.8	>3.0

Water chlorination involves establishing free chlorine residuals through the destruction of naturally present ammonia if necessary, and maintaining it throughout the system. In treating surface water, this may involve prechlorination at breakpoint dosages for the first process step, postchlorination to establish residuals leaving the treatment plant, and rechlorination at selected points within the distribution system to retain adequate the free residuals. Large dosages of chlorine applied during treatment may result in a large amount of residuals that are objectionable or undesirable for industrial water uses.
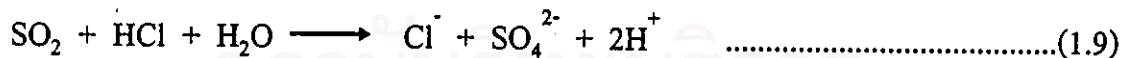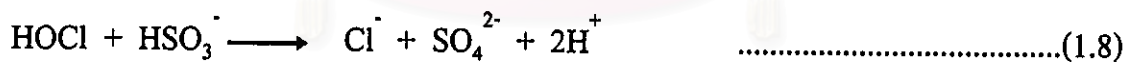
1.2 Dechlorination

Permeable membranes, such as cellulose acetate which is often used in reverse osmosis (RO) treatments, are often susceptible to degradation by dissolved chlorine. The same is true for devinylbenzene which is often used to crosslink ion-exchange resins[3]. The dechlorination must be used in combination with RO or ion exchange .

Dechlorination is a process of removing chlorine residuals remaining after chlorination in order to reduce the toxic effects of chlorinated effluents discharged to receiving waters or to be used for reuse application.

Dechlorination can be done by the use of sulfur dioxide, adsorption with activated carbon or utilizing the principle of electrochemical oxidation reduction.

### 1.2.1. Dechlorination by Uses of Sulfur dioxide

In most situations, sulfur dioxide dechlorination is a reliable process in wastewater treatment. When sulfur dioxide is added to a wastewater, the following reactions occur[1]

$$SO_2 + H_2O \longrightarrow HSO_3^- + H^+ \quad \dots\dots\dots\dots\dots\dots\dots (1.7)$$

$$HOCl + HSO_3^- \longrightarrow Cl^- + SO_4^{2-} + 2H^+ \quad \dots\dots\dots\dots\dots (1.8)$$

$$SO_2 + HCl + H_2O \longrightarrow Cl^- + SO_4^{2-} + 2H^+ \quad \dots\dots\dots\dots (1.9)$$

Reactions of sulfur dioxide with chlorine is nearly instantaneous. Therefore, the process requires perfect mixing at the point of application.

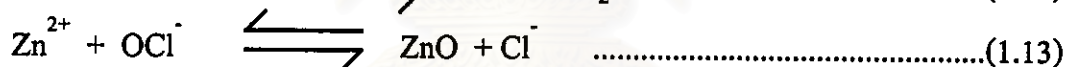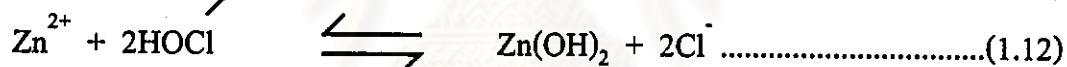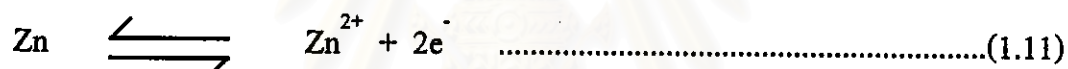### 1.2.2. Dechlorination by uses of Adsorption on Activated Carbon .

When an activated carbon is used for dechlorination, the following reactions occur.[4]

$$C_{(s)} + OCl^-_{(aq)} \longrightarrow C_nO + Cl^-_{(aq)} \quad \dots\dots\dots\dots\dots\dots(1.10)$$
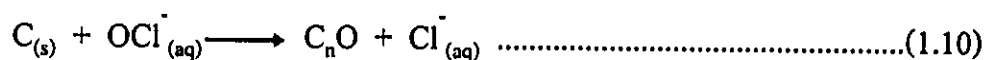
Free chlorine reacts within the porous carbons to form interior surface oxides via adsorption mechanism and reduction reactions releasing chlorine ions in the process.

1.2.3. Dechlorination by Utilizing Principles of Electrochemical Oxidation.

Chlorine can be eliminated by utilizing principles of electrochemical oxidation reduction.[3] Redox alloy, called KDF, consists of high purity zinc and copper. KDF forms spontaneous oxidation reductions with many contaminants. Conversion of chlorine to chloride by KDF is suggested to occur as follows[4].

$$Zn \rightleftharpoons Zn^{2+} + 2e^- \quad \dots\dots\dots\dots\dots\dots(1.11)$$

$$Zn^{2+} + 2HOCl \rightleftharpoons Zn(OH)_2 + 2Cl^- \quad \dots\dots\dots\dots(1.12)$$

$$Zn^{2+} + OCl^- \rightleftharpoons ZnO + Cl^- \quad \dots\dots\dots\dots(1.13)$$

1.3 Measurements of Chlorine Contents

Chlorine residual can be measured by a chemical analysis method, oxidation reduction potential instrument or spectrophotometry. Most methods for the determination of free or combined available chlorines are based on reactions with reducing agents. The ortholidine - arsenite (OTA) method[2] test differentiates and measures both free and combined chlorine residuals. Ortholidine is an organic compound oxidized in acid solution by chlorine, chloramine and other oxidizing agents to produce a yellow - colored compound. The intensity of color development is proportional to the amount of chlorine residuals. This color can be measured photometrically and reading converted to the proper chlorine value by referring to a

calibration curve prepared by treating known chlorine concentrations in the same manner as the unknown samples.[5]

1.3.1 Spectrophotometry

For a spectrophotometer, such as model DR/2000 manufactured by "HATCH" , the DPD Method which is adapted from Standard Methods for the examination of water and wastewater, is used for measurement of Chlorine residual. The procedure is equivalent to USPA method 330.5 for wastewater and Standard Method 4500-Cl G for drinking water. The procedure including using DPD total chlorine powder pillow reagent reacts with 25 ml sample for 3 minutes. The pink color developed by this reaction is measured using wave length of 530 nm. The accuracy is 0.01 mg/l.(see in appendix A1)

1.3.2 Oxidation Reduction Potential Measurement

Oxidation Reduction Potential (ORP) value is an indicator of the oxidation ability of a solution and is related to the concentration of oxidizers and their activity or strength. Usually, pure water has an ORP value of between 200 and 300 mV. This range is consider to be "zero" or a reference point, while an additional oxidizing chemicals will result in a value which is greater than 300 mV.

When an ORP sensor is placed in water containing a sanitizer-such as chlorine, bromine or ozone, which is also an oxidizer, it acts like a small battery and creates a small electric potential which is measurable. The value of this potential varies with the types of sanitizers and the concentrations.

The half cell oxidation reduction potential Eo for HOCL at 25 $^\circ$C is :

$$HOCL + H + 2e^- \longrightarrow Cl^- + H_2O \qquad (1.14)$$
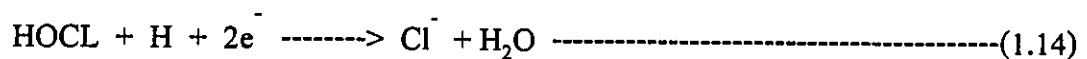
$$Eo = 1.49V.$$

If one assumes that Cl^- is in the reduced state for chlorine, the variation of ORP for HOCl is given by the following expression:

$$ORP = Eo + (0.059/N)\log(HOCl/Cl^-) - Eh \text{ -----------------------------}(1.15)$$

Where N is the number of electrons and Eh is the potential of the reference electrode. The actual relationship of ORP is, in fact, complex due to the various oxidation and reduction state of chlorine. However, one can find that ORP increases logarithmically with increasing HOCl concentration.

HOCl is a weak acid. As the pH increase, it dissociates to produce the hypochlorite ion and a hydrogen ion :

$$HOCl \text{ <---------------------> } OCl^- \quad + \quad H^+ \text{ ------------------}(1.16)$$

hypochlorous Acid   Hypochlorite Ion   Hydrogen Ion

OCl^-, being consistent with its much lower activity as a sanitizer, has a much lower ORP value than HOCl

$$OCl^- + H_2O + 2e \text{ -------------> } Cl^- \quad + \quad OH^- \text{ ----------------}(1.17)$$
$$Eo = 0.9V.$$

The expression for the ORP of the hypochlorite ion OCl^- is similar to that of HOCl in equation (1.15). Since Eo is lower, the ORP values are much lower than those of HOCl. As a result, when HOCl is present, it tends to "mask" the ORP of OCl^-. Consequently, as the pH of a chlorine-containing solution increases, the oxidizing capability decreases and is reflected directly in the ORP reading. This is

why the ORP sensor is said to read only the HOCl. The ORP value reading is converted to the proper chlorine value by referring to a calibration curve prepared by reading ORP of known chlorine concentrations

However, chlorine solution is not stable. It decomposes more rapidly at high concentrations and is affected by exposure to light or heat. For instance, a 16.7 percent solution stored at 26.7 ^{o}C will lose 10 percent of its strength in 10 days, 20 percent in 25 days and 30 percent in 45 days.[1] Therefore, the chlorine content of the solutions, particularly weak solutions, will rapidly decrease. Agitation will accelerate the reduction of chlorine present in such solutions. It is recommended that chlorine determinations must be measure immediately after sampling, and must be avoided excessive light and agitation.[5]