



CHAPTER 2

BACKGROUND AND LITERATURE REVIEWS

2.1 Trihalomethanes (THMs)

2.1.1 Background and Regulatory History

In 1974, the Dutch scientist Johannes Rook was the first to identify chloro and bromotrihalomethanes (THMs), the first class of halogenated disinfection by products (DBPs) discovered in chlorinated drinking water (Rook, 1974). A year later, in 1975, the United States Environmental Protection Agency (US.EPA) conducted a survey which identified chloroform as being dominant in most chlorinated drinking water (Symons et al., 1975). Chloroform was identified in 1976 by the National Cancer Institute as a suspected human carcinogen (National Cancer Institute, 1978), which led the US.EPA to set a maximum contaminant level (MCL) for total THMs (TTHMs) at 0.10 mg/L (US.EPA, 1997). This standard applied to systems serving over 10,000 people. Due to wide occurrence and potential health risks of DBPs, the USEPA proposed the Disinfectants/Disinfection By-Products (D/DBP) Rule in two stages. Stage 1 of the D/DBP Rule was proposed in 1994 (US.EPA, 1994). It proposed TTHM MCLs of 0.080 mg/L. Stage 2 of the D/DBP Rule was proposed in 1994, which required even lower MCLs for DBPs than Stage 1 (0.040 mg/L).

2.1.2 Chemistry of Trihalomethanes (THMs)

THMs are organohalogen compounds that are named as derivatives of methane when three out of the four hydrogen atoms are substituted by three halogen atoms such as chloride (Cl), bromine (Br), iodine (I) or a combination thereof. THM has a general formula, CHX_3 , where X is the halogen atom.

THMs are formed during the reaction between a chemical disinfectant (such as chlorine) and natural organic matter (NOM; as referred to as precursors) in water. The primary biochemical ancestors of THM identified by many researchers are

humic substances including humic acid and fulvic acid (Rook, 1976; Trussell and Umphes, 1978; Oliver and Lawrence, 1979), algal materials mainly the chlorophyll-a, algal biomass and their extracellular products (Hoenh et al., 1984; Oliver and Shindler, 1979), proteins assortment of aromatic substance (Copper et al., 1985) occurring naturally in the water. These materials also contribute to the natural color of the water.

Bromine (Amy et al., 1983) was also identified as precursors, since its presence in chlorinated water may be oxidized by chlorine to form hypobromous acid (HOBr), which led to the formation of brominated THM species. Iodine, to a lesser extent, was also observed by Gould et al. (1985).

Four THM species of concern in drinking water are chloroform, bromdichloromethane, dibromodichloromethane and bromoform.

2.1.2.1 Chloroform

The basic chemical and physical data of Chloroform or trichloromethane (CHCl_3) is shown in Table 2.1. Chloroform has a chemical structure as follows:

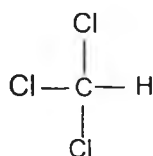


Table 2.1 Basic chemical and physical data of chloroform

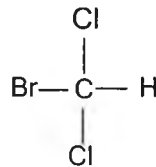
Empirical Formula:	CHCl_3
Molecular weight:	119.37 g/mol
Specific gravity:	1.472 g/cm ³
Boiling point:	61 °C
Melting point:	-63 °C
Solubility	in water: 8.1 g/L

(Source: Ghazali, 1989)

Chloroform is not only a central nervous system depression, but also a THMs with hepatotoxicity, nephrotoxicity, teratogenicity and carcinogenicity (USEPA, 1998)

2.1.2.2 Bromodichloromethane

Bromodichloromethane or dichlorobromomethane (CHCl_2Br) has a chemical structure as follows:



Its chemical and physical characteristic are shown in Table 2.2

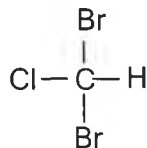
Table 2.2 Basic chemical and physical data of bromodichloromethane

Empirical Formula:	CHCl_2Br
Molecular weight:	163.82 g/mol
Specific gravity:	1.472 g/cm ³
Boiling point:	90.1 C
Melting point:	-57.1 °C
Solubility	Insoluble in water

(Source: Ghazali, 1989)

2.1.2.3 Dibromochloromethane

Dibromochloromethane or chlorodibromomethane (CHClBr_2) has a chemical structure as follows:



It is a clear, colorless and heavy liquid with specific gravity of 2.38. Other characteristics are shown in Table 2.3.

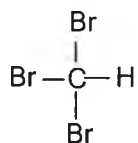
Table 2.3 Basic chemical and physical data of dibromochloromethane

Empirical Formula:	CHCl ₃
Molecular weight:	208.29 g/mol
Specific gravity:	2.38 g/cm ³
Boiling point:	120°C
Melting point:	-63 °C
Solubility	4.75 g/L

(Source: Ghazali, 1989)

2.1.2.4 Bromoform

Bromoform or tribromomethane or methyl tribromide (CHBr₃) has a chemical structure as follows:

**Table 2.4 Basic chemical and physical datas of bromoform**

Empirical Formula:	CHBr ₃
Molecular weight:	257.73 g/mol
Specific gravity:	2.894 g/cm ³
Boiling point:	150°C
Melting point:	8.3 °C
Solubility	Insoluble in water

(Source: Ghazali, 1989)

2.1.3 Possible Reaction Pathway of THMs in Water Treatment

Trussell and Umphres (1978) revealed the classical reaction of aqueous hypohalites with methyl ketones or compounds capable of oxidizing methyl ketone to yield haloforms. The pattern of reaction is the replacement of hydrogen by achlorine alpha, to a carbonyl group, followed by eventual hydrolysis to produce CHX_3 .

During water treatment, (Reckhow and Singer, 1990) summarized a series of possible reactions that the basic steps by which chloroform can be produced, as follows:-

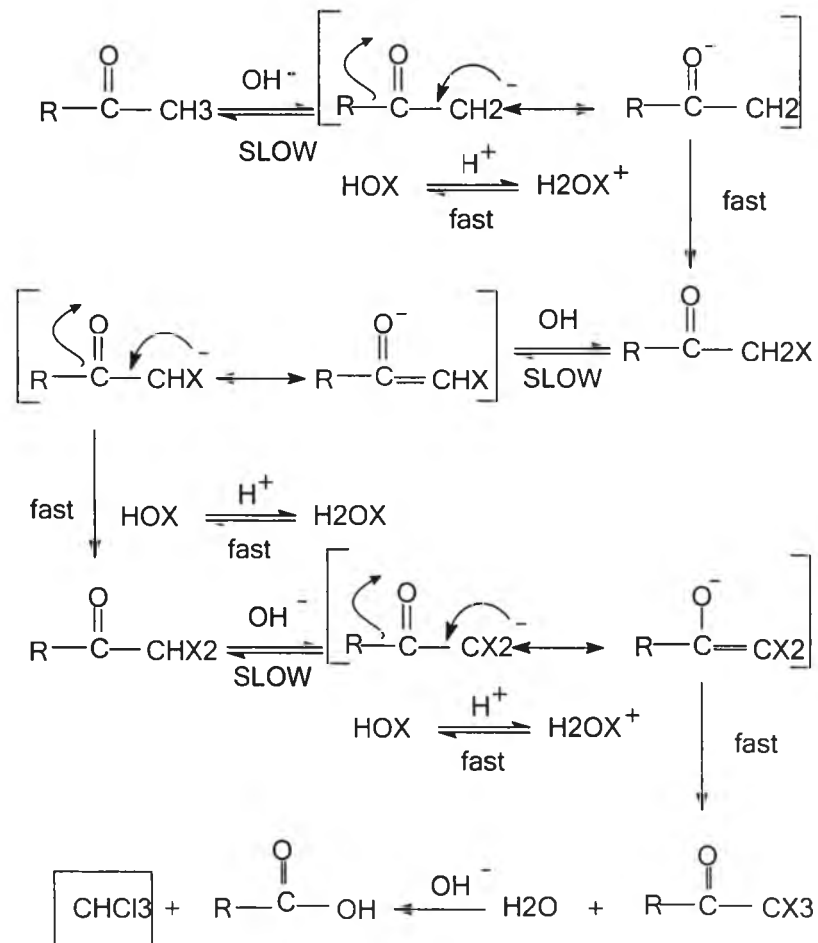


Figure 2.1 Haloform Reaction Pathway

National Environmental board (1984) demonstrated a series of reactions of chloroform that may be produced during water treatment. The diagrams are shown in Figure 2.2.

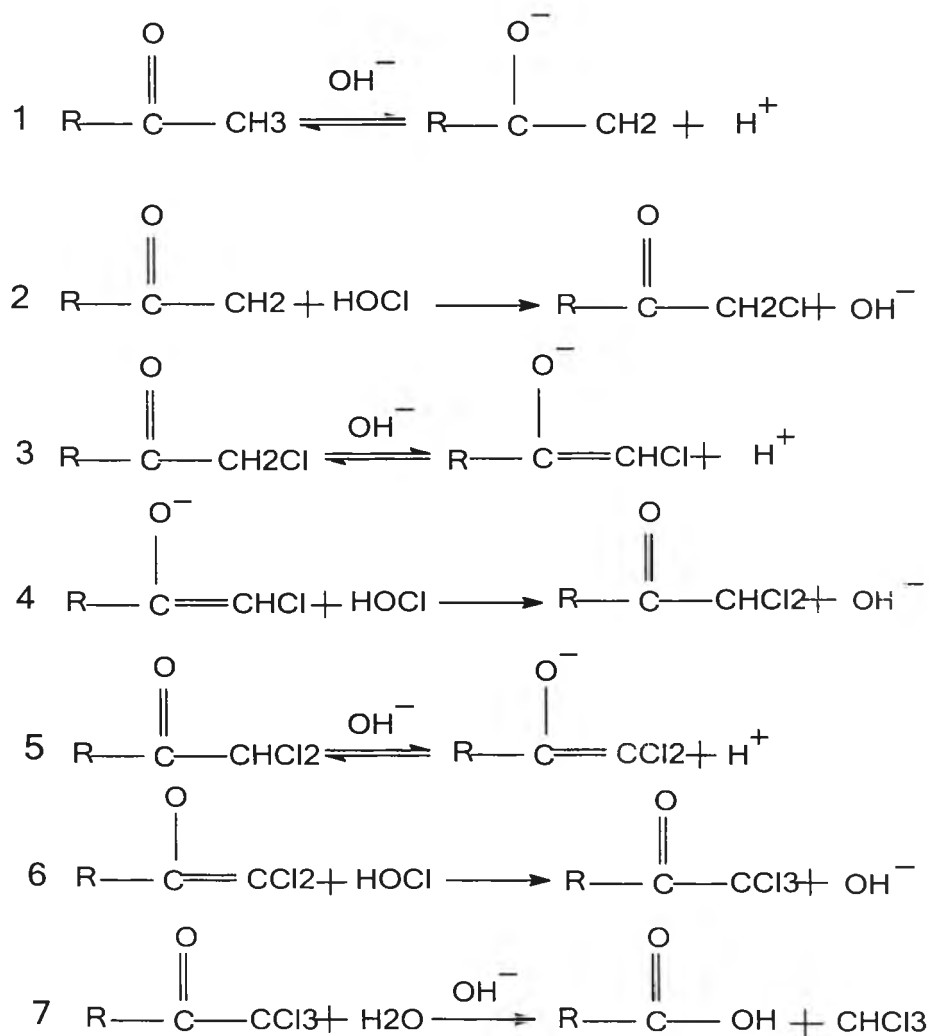


Figure 2.2 Basic steps of reaction of chloroform that may be produced during water treatment

2.1.4 Trihalomethanes Formation Potential (THMFP)

Definition of Terms

Total trihalomethanes (TTHMs) are the sum of all four compounds concentration, which include chloroform, dichlorobromomethane, dibromochloromethane and bromoform, produced at any time T (usually day).

$TTHM_0$ is the total THMs concentration at the time of sampling. It can have range from non-detectable to several hundred micrograms per liter if the sample has been chlorinated.

$TTHM_7$ is the total concentration of all four THMs compounds produced during the reaction of sample precursors with excess free chlorine over a 7-day reaction time at standard reaction condition, which are as follows: free chlorine residual at least 3 mg/L and not more than 5 mg/L at the end of a 7-day reaction (incubation) period with a sample incubation temperature of $25 \pm 2^\circ\text{C}$, and pH controlled at 7 ± 0.2 with phosphate buffer.

THMFP or $\Delta TTHMFP$ is the difference between the final $TTHM_T$ concentration and the initial $TTHM_0$ concentration. For the sample, which does not contains chlorine at the time of sampling, $TTHM_0$ will be closed to zero. Therefore, the term THMFP may be used. The sample that contains chlorine at the time of sampling, $TTHM_0$ will be detected. Therefore, the term $\Delta TTHMFP$ may be used when reporting the difference between TTHM concentration.

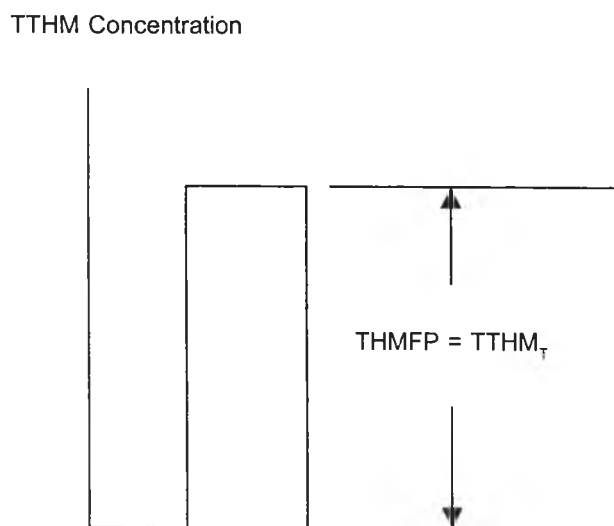


Figure 2.3 Definition used in the formation potential test of a sample without free chlorine at the time of sampling.

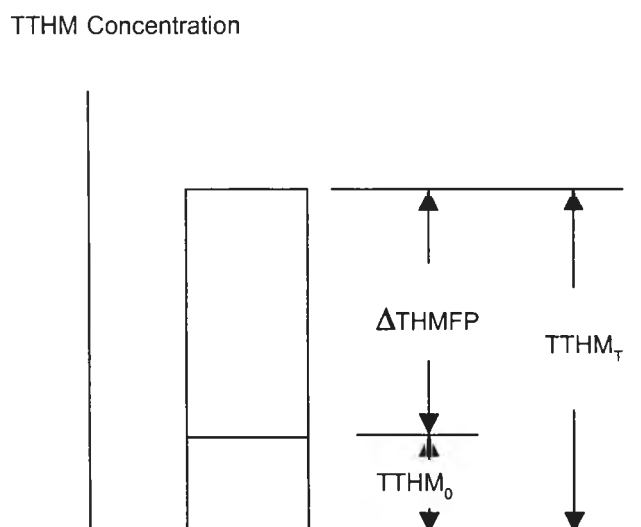


Figure 2.4 Definition used in the formation potential test of a sample that with free chlorine at the time of sampling.

Sakornarun (1987) did a comparative study of THMs content in water as a result of pre-chlorination and post chlorination and a study the relationship between TOC and THMs produced. Water samples from 4 sources, Chao Phraya River in Bangkok and in Ayudtaya Province, and the Klong Prapa at Samsen and Bangken were collected and treated with chlorine dosages of 3, 5, 7, 10, 15, and 20 ppm. and contact times of 1, 3, 6, 12, and 24 h. THMs contents were analyzed before and after chlorination. Headspace method and GC/ECD was used to analyze THMs. The results showed that THMs contents in treated water as treated the post chlorination were significant less than those treated by pre-chlorination. Coagulation by alum reduced TOC by 34.30 percent and THM by 47.86 percent in raw water.

El-Shahat, Abdel-Halim and Hassan (1998) evaluated trihalomethnes in water treatment plants' output in Cairo. Mean values of THMs in water treatment plants outputs (Sept. 1991- Dec. 1991) ranged from 31.70 to 61.41 $\mu\text{g/L}$. Moreover, mean values of THMs in water treatment plants outputs (Jan. 1992 - August 1992) ranged from 19.19 to 42.30 $\mu\text{g/L}$.

El-Shahat et al. (2001) investigated THMs in various stages of the water treatment process in Tebbin, Rod El-Farag and Mostorod water treatment plants during summer and water seasons. Stages of the water treatment process that were investigated consist of raw water in, clarifier, filter effluent and finished water. The results showed that the highest THMs concentration occur in finish water and its range between 41.70 and 54.50 $\mu\text{g/L}$ in summer, 29.00 and 34.90 $\mu\text{g/L}$ in winter. Moreover, THMs concentration in filter effluent is higher than in clarifier and THMs concentration in clarifier is higher than in raw water.

2.1.5 Factors Influencing THMs Formation

Many studies have concluded that THM formation in drinking water depends upon various factors, such as pH, concentration of precursors, concentration of chlorine, temperature, the most distinctly, and reaction time.

2.1.5.1 pH

Rook (1976) suggested that THM formation increased evidently at pH values from 8 to 10 whereas in the range of pH 1 to 7 have less influence to the THM formation, a feasible variation range during chlorinating.

Stevens et al. (1976) conducted an experiment with a wider pH range from 6.5 to 11.5. The results show that the rate of formation to chloroform increased with the increase in pH. They explained that this was due to the increase in the humic acid reaction rate, since the rate-determining step of the classical haloform reaction was enolization (mechanistic interpretation of the bromination) of a ketone.

2.1.5.2 Precursor Concentration

Since the THM formation is a result of the reaction between chlorine and the THM precursors, it is obvious that the precursor concentrations would influence the THM concentrations. Rook (1976), in his series of experiments varied the concentrations of the organic precursors in order to study if TOC should be reduced

before chlorinating. In this regard, it was found that the chloroform production from organic matter is linear in concentration up to 250 mg/l TOC.

2.1.5.3 Chlorine Dose

Chlorine dosage is one of the most important factors influencing THM formation. Trussell and Umphres (1978) conducted a laboratory test with synthetic water prepared by adding 10 mg/L of humic acid, 1 mg/L of NH_3Cl (as NH_3) and 10 mg/L of standard pH 7 buffer to demineralized water (TOC 0.2 mg/L). Different amounts of chlorine were added to various portions. After 2 hours of contact time, the results show that higher THM concentration occurred within a certain range of chlorine precursor to form THM as chlorine has been used up to react with ammonia, bacterial disinfecting, etc.

2.1.5.4 Temperature

The effect of temperature on the rate of THM formation was investigated by Stevens et al. (1976) using the Ohio River water collected in winter to summer. The result showed that the temperature differentials could easily account for most of winter to summer variations in chloroform concentration with a three to four days chlorine contact time.

2.1.5.5 Reaction Time

Reaction time is among the major factors influencing the THM formation. Recknow and Singer (1984) ran a few sets of experiments. One of these experiments was to study the formation of these chlorinated products as a function of the reaction time. They found that by varying the chlorine contact time, chloroform and total THM increases rapidly in the first few hours and then slow to a generally steady rate of increase. This result is quite similar to that from previous researchers, which concluded that the active rate of reaction is within the first few hours of contact time.

2.1.6 Empirical Kinetic Model of THM Formation

Early research indicated that “the THM reaction is one of the slowest reactions of interest to the water utility practitioner”. The formation reaction occurs over several hours and some systems exhibited significant increases after 24 hours of reaction. The kinetics of THM formation is dependent on many factors such as $[H]^+$, $[Cl_2]$, precursor, and temperature. On the other hand, there is evidence that THM formation occurs within 2 hours. However, it is difficult to follow kinetics with precision because there are competing reactions for the chlorine.

A kinetic equation for the THM reaction is :

$$\frac{d[Cl_2]}{dt} = -k_1[Cl_2][TOC] \quad (2.1)$$

Where it is assumed that the rate of chlorine consumption is dependent on its content and precursor content is expressed as TOC. Furthermore, if it is assumed that the $[TOC]$ is not significantly reduced, then:

$$\ln \frac{[Cl_2]_t}{[Cl_2]_0} = -k_1[TOC]t \quad (2.2)$$

This equation represents a first-order reaction with respect to chlorine residual. Another approach assumes that the rate of THM formation is related to residual chlorine to the first power

$$\frac{d[THM]}{dt} = -\frac{dC}{dt} = k_2[Cl_2][C]^m \quad (2.3)$$

Where m is the order of reaction with respect to $[C]$, the precursor concentration. When m is 3, a third-order reaction gives “a good fit”.

One intent of kinetic studies is to develop predictive models for the formation of DBPs from various precursors. For example, several mathematical equations were used to formulate an overall model for predicting chloroform from humic acid in terms of time, initial total organic carbon (TOC) initial chlorine to TOC ratio, reaction temperature, and reaction pH. All of these reaction components of the model are especially relevant in the operation of a water treatment plant and enforcement of the THM MCL. A generalized reaction is:



This is a simple CHCl_3 formation reaction based on the absence of both bromide as a reactant and brominated haloforms as products. Kinetically, three mathematical models describe the role of each component of the reaction:

$$[\text{CHCl}_3] = k_a t^z \quad (2.4)$$

$$[\text{CHCl}_3] = k_b \frac{[\text{Cl}_2]^y}{[\text{TOC}]} t^z \quad (2.5)$$

$$[\text{CHCl}_3] = k_c [\text{TOC}]^x t^z \quad (2.6)$$

Where $[\text{CHCl}_3]$ is the chloroform concentration, $\mu\text{g/L}$; t is the reaction time, hours; $[\text{TOC}]$ is the initial TOC concentration, mg/L ; $[\text{Cl}_2]/[\text{TOC}]$ is the initial Cl_2 to TOC ratio; x , y , and z are empirically derived constants; and k_a , k_b , and k_c are empirical reaction rate constants. In turn, these three submodels were incorporated into an overall model:

$$[\text{CHCl}_3] = K[\text{TOC}]^x \frac{\text{Cl}_2^y}{\text{TOC}} t^z \quad (2.7)$$

Where K is an overall reaction constant that includes reaction constants for effects of pH and temperature. In this empirical study, a multiple linear regression

technique was employed to obtain the reaction constants and the exponents x , y , and z in the above equations. This resulted in :

$$\ln[\text{CHCl}_3] = \ln K + x \ln[\text{TOC}] + y \ln \frac{\text{Cl}_2}{\text{TOC}} + z \ln t \quad (2.8)$$

Regression of the appropriate experimental data yielded these values of K , x , y , and z of 16.8, 0.95, 0.28, and 0.22, respectively, with a correlation coefficient of 0.99. Figure 2.5 shows the natural log-log plot of measured versus predicted CHCl_3 concentrations based on Equation 10 and the above values of K , x , y , and z obtained from the regression. Undoubtedly, this approach can be used for other precursors and DBPs that would be unique to given water supply system.

An empirical rate equation was developed for the formation of THMs from chlorination of synthetic humic acid solution and several river and lake waters in Japan. This equation was obtained:

$$[\text{THM}] = K(\text{pH} - a)[\text{TOC}][\text{Cl}_2]_0^m t^n \quad (2.9)$$

Where $[\text{THM}]$ is the concentration of total THM after 1 hours $[\text{TOC}]$ and $[\text{Cl}_2]_0$ are the concentrations of total organic carbon and chlorine dosage; K is the overall reaction rate constant; and a , m , and n are parameters. The latter values, obtained empirically for humic acid, were 8.2×10^{-4} ($\text{l}^m \text{mg}^{-m} \text{h}^{-n}$), 2.8, 0.25, and 0.36, respectively. In this study, THM formation was followed over a reaction period of 50 hours wherein $[\text{THM}]$ peaked at about 10 h, but slowly continued to increase afterward.

Additional empirical models for predicting THMFP and kinetics of formation are found in reference 68. Linear and nonlinear multiple regression models were employed for THM formation during the chlorination of natural waters. These models, according to the authors, can serve as an accurate predictor of 96-h and 2-h THMFP levels in waters subjected to alum coagulation, activation carbon adsorption, or ozone oxidation.

Most of the kinetic studies cited above have employed the relatively high-molecular-weight model compounds of humic and fulvic acids. The rate of appearance of CHCl_3 and other DBPs is “slow,” with reaction times of 50 to 175 hours. On the other hand, it was evident that aspartic in experiments was quickly formed after chlorination. Approximately 300 $\mu\text{g/L}$ of DCAN and 200 $\mu\text{g/L}$ chloral were formed within structurally less complex precursors by which their DBPs could be produced at relatively rapid rates and within hydraulic detention times of water treatment plants.

2.1.7 Toxicity of THMs

THMs are chemicals with various industrial uses. Excessive exposure to each of them can cause adverse health effects, principally on the central nervous system. In industrial settings, exposure is usually by inhalation of vapor, but direct skin contact with their liquids also can have adverse local and systemic effects. Exposure to THMs from drinking water is typically at levels very much lower than the exposure which might occur from the industrial use of individual THMs. Available studies indicate that the gastrointestinal absorption of all the THMs is high.

In 1975, it was recognized that the chlorination of water produced a number of by-product contaminate including THMs. Subsequently, many epidemiological studies have been conducted to investigate the association between the consumption of chlorinated drinking water and cancer. While the results of these studies have been inconsistent, some studies have indicated an association between the consumption of chlorinated drinking water and an increased risk of colon, rectal and bladder cancers. However, many of these studies have been of ecological design and studies of this type can not show a cause and effect relationship.

Mammalian responses to chloroform include effects on central nervous system, hepatotoxicity, nephrotoxicity, teratogenicity and carcinogenicity. A comprehensive carcinogen test programme by the U.S. NCI on diverse chorohydrocarbon, both fully saturated or with an ethnlenic bond, uniformly induced liver tumors in male and female mice, give evidence of severe nephrotoxicity and in several instances had a low yield carcinogenic effect on the kidney of Osborne-

Mendal Strain rat. On the other hand, bromohydrocarbons are genotoxic and in addition to causing liver tumors in mice also induce forestomach tumors in rats and mice rather quickly in high yield.

Tuthill and Moore (1980) stated that a number of recent epidemiological studies have reported the association of chlorination or elevated THMs levels in drinking water with increased risk of cancer of several sites including the bladder, stomach, rectum, large intestine, esophagus, breast and lung.

In 1981, Cotruvo reported that it has been reported since 1945 that chloroform induced carcinogenicity. Hepatomas were produced in female Strain A mice given a repeated dose of 0.145-2.32 mg for a four month period.

In the same year Cotruvo also reported that in a bioassay performed by NCI, rat and mice of both sexes were fed of chloroform 90-200 mg/kg-d(rats) and 138-147 mg/kg-d(mice), five days each week for 72 weeks. Hepatocellular carcinomas were observed in male and female mice at both the high and low doses at a statistically significant level.

Chloroform is the most common THMs found in chlorinated water and can be rapidly adsorbed on oral and intraperitoneal administration and subsequently metabolized to carbon dioxide chloride ion, phosgene and other unidentified metabolites in test animals. The most toxic substance in the metabolism of chloroform seems to be phosgene (Cotruvo, 1981).

In-vitro mutagenicity studies using *Salmonella typhimurium* were conducted because this test has been found in a number of cases to correlate with carcinogenicity from in vivo bioassays. Chloroform was not mutagenic in this test, but bromodichloromethane, dibromochloromethane and bromoform all were. In vitro biochemical studies have detected 2-oxothiazolidine-4-carboxylic acid as a common metabolite from chloroform, deuteriochloroform and bromoform presumably formed by reaction of a phosgene like intermediate with cysteine. These studies correlated the extent of the hetatotoxic effect and the depletion in the liver with the rate of metabolism (Cotruvo, 1981).

Cotruvo also stated in the same year that in his a study, which measured chloroform levels in blood among groups of individuals drinking chlorinated water and non-chlorinated water, levels were significantly higher in the group consuming chlorinated water.

The studies above indicated that THMs have the potential health effects on experimental animal in high doses, but the health effect to THMs in low concentration as present in drinking water are now not clear. It should be noted that those effects showed in animals may be have the same effect to mankind.

The EPA computed U.S. human up take levels of THMs in milligramme per year from air, food and drinking water employing as number of assumption as shown in the Table 2.5.

Table 2.5 Human Uptake of Chloroform and Trihalomethanes from drinking water, Food and Air.

Chemical	Exposure level mg/l, mean and (range)		
	Drinking Water	Food	Air
Chloroform	64 (0.73-343)	9 (2-15.97)	20 (0.41-204)
Trihalomethanes	85 (0.73-572)	-	-

Under extreme condition of high water contribution drinking water contributed 79 % of total uptake (Cotruvo, 1981).

Cotruvo (1981) stated that the human health effect observed in accidental, habitual and occupational exposures to chloroform indicated that effects are similar to those found in experimental animal. These include effect on the central nervous system, liver and kidneys.

The acute toxicity, LD₅₀ of trihalomethanes is shown in table 2.6. Acute chloroform exposure may result in health by respiratory arrest. The primary toxic response at low level of exposure is hepatotoxicity leading to fatty liver and centrilobular necrosis. Kidney damage may also occur in animal after acute poisoning in the convoluted tubules, but it may also effect the epithelium of Henles's loops (NEB, 1984).

Table 2.6 Acute Toxicity of Trihalomethanes

Compound	No. of rats Lethal time			LD50 mg/l p=0.05	
	M	F	day	M	F
Chloroform	90	90	1-9	1120 (789-1590)	1400 (1120-1680)
Bromodichloromethanes	70	90	1-6	450 (326-621)	900 (811-990)
Dibromodichloromethanes	80	80	1-5	800 (667-960)	1200 (945-1524)
Bromofrom	80	70	1-9	1400 (1205-1595)	1550 (1165-2062)

2.2 THM Precursors

2.2.1 THM Precursors in Nature

THM precursors consist primarily of NOM. Limnologists refer to precursors and nutrients in natural waters as either allocthonous (derived from the surrounding watershed, including land and sub-surface waterways) or autochthonous (derived from within the water body). Watershed run-off is a major contributor to allocthonous humic materials; dissolved and particulate organic substances are transported to a water body during run-off events (Cooke and Carlson, 1989). Algae and macrophytes are sources of organics within surface water bodies (Cooke and

Carson, 1989). Randtke (1988) noted that the mean non-volatile TOC concentration reported in a study for lakes and reservoirs was 3.33 mg/L, versus 1.89 mg/L for groundwater.

The organic carbon of natural water is comprised of humic and non-humic substances. Humic substances include humic and fulvic acids, while non-humic substances include hydrophilic acids, proteins, carbohydrates, carboxylic acids, amino acids, and hydrocarbons (Thurman, 1985 ; Amy, 1993).

Aquatic humic substances are yellow to brown colored, polymeric acids which can be leached from soil and sediments, and are known to be natural by-products of vegetative degradation (Thurman, 1985). In most surface waters, the concentration of humic substances ranges from 100 $\mu\text{g/L}$ to 4 mg/L, with concentrations in bogs and marshes sometimes exceeding 100 mg/L (Thurman, 1985). Humic substances are comprised of humic and fulvic acids, which are differentiated by ultraviolet light absorbance (UVA), specific UVA (SUVA), and molecular weight ranges.

The UVA of humic materials can provide insight into the nature of the organics present, and the potential THM formation. As noted by Edzwald et al. (1985), humic aromatic compounds and molecules with conjugated double bonds absorb UV light, whereas simple aliphatic acids, alcohols, and sugars do not absorb UV light. Reckhow et al. (1990) measured the UVA and THM formations of the humic and fulvic fractions of five different sources. Humic acids had greater UVA, more aromatic rings, and a higher molecular weight than fulvic acids. As the aromatic content increased (as in humic acids) the percentage of chlorine incorporation (i.e., THM formation) also increased.

SUVA (which is the UVA divided by the dissolved organic carbon concentration) can be used as an indicator of the ability of coagulation (or softening) to remove THM precursors. Water having a high SUVA ($\text{SUVA} > 3 \text{ L/mg-m}$) have been found to contain organic matter that is more humic-like in character, higher in apparent molecular weight (AMW), and more readily removed by coagulation

(Edzwald, 1993) whereas lower USVA values ($< 3\text{L/mg}\cdot\text{m}$) indicate the presence of organic matter of lower AMW that is more fulvic-like in character and more difficult to remove. Shorney et al. (1996) found that DOC removal was significantly higher for source waters having SUVA values greater than $4\text{L/mg}\cdot\text{m}$. Coagulation and softening are expected to result in a lowering of the SUVA value for any given water, since the less removable organic matter remaining in the water should exhibit a lower SUVA than the material that is removed.

The molecular weights of fulvic acids typically range from 500 to 2,000 a.m.u. (Thurman, 1985; Amy et al., 1992). Fulvic acids have a higher charge density and are less amenable to coagulation by charge neutralization (Amy et al., 1992). Fulvic acids are also more prevalent and more soluble than humic acids. The SUVA of fulvic acids at 254 nanometers (nm) ranges from 2.9 to $4.3\text{L/mg}\cdot\text{m}$ (Reckhow et al., 1990).

Humic acids have a molecular weight greater than 2,000 a.m.u., and usually less than 100,000 a.m.u. The SUVA of humic acids range from 4.8 to $7.4\text{L/mg}\cdot\text{m}$ (Reckhow et al., 1990).

Non-humic substances, such as algae and their extracellular products, have been shown to be precursors to THMs (Morris and Baum, 1978; Oliver and Shindler, 1980). Oliver and Shindler (1980) observed faster reaction kinetics between chlorine and algae than between chlorine and aquatic humic materials. Their results suggest that algae in surface waters may be a major contributor to THM production.

Humic acids have generally been found to be more reactive with chlorine than fulvic acids. There is also evidence that the humic fraction produces greater concentrations of HAAs and THMs than the non-humic fraction.

The molecular weight of precursors has also been correlated with THM formation potential (THMFP). Bell et al. (1996) indicated that organic molecules with molecular weights greater than 1 kilodalton (kd) contributed more THMFP than did the organics having molecular weights less than 1 kd. Recent work by Shnha et al. (1997) showed that THM precursors were predominately larger molecular weight humic materials, whereas the HAA precursors were large molecular weight humic and non-humic materials.

NOM plays a role in many aspects of water treatment. NOM can impart color to water and is capable of forming complexes with metals such as iron. It can serve as a substrate for microbial growth and can exert significant oxidant demand, thereby interfering with both oxidation and disinfection during drinking water treatment. Oxidation of NOM can release carbon dioxide, however, most of the oxidized molecules remain as dissolved compounds with lower molecular weights and oftentimes less color. Depending on the concentration and type of NOM, the acidity of water can also be affected.

2.2.2 Surrogate Parameter for Monitoring THM precursors

To describe the characteristic of NOM, surrogate parameters must be used because no single analytical technique is capable of measuring the widely varied characteristics of NOM. Commonly used NOM surrogates include TOC, DOC, ultraviolet absorbance at wavelength of 254nm (UV-254) and THMFP. Moreover, THMFP removal is also present to highlight any difference between TOC and THMFP removals (US.EPA, 1999).

2.2.2.1 Total Organic Carbon(TOC)

The organic carbon in water and wastewater is composed of a variety of organic compounds in various oxidation states. However, TOC is independent of oxidation state of organic matter and does not measure other organically bound elements such as hydrogen, nitrogen, and inorganic. TOC are defined as all carbon atoms covalent bonded in organic molecules.

For removal of DBPPs, TOC is commonly used as a surrogate parameter for DBPPs. Therefore, the percentage TOC removal is correlation to the percentage removal of DBPPs. The USEPA proposed the percentage TOC required for enhanced coagulation and softening. It will depend upon the TOC and alkaline concentration in raw water. The detail are shown in Table 2.8 (US.EPA, 1999).

Table 2.7 Percentage TOC removal requirements for enhanced coagulation and softening

Source Water TOC Mg/L	Source Water Alkalinity (mg/L as CaCO ₃)		
	0-60	>60-120	>120*
2.0-4.0	35	25	15
4.0-8.0	45	35	25
>8.0	50	40	30

* System which shown must achieve the percentage removals in this column
(Source: US.EPA 1999)

2.2.2.2 Dissolve Organic Carbon (DOC)

Dissolved organic carbons are defined as the fraction of TOC that passes through a 0.45- μ m-pore-diam filter (Standard method, 1995).

Organic carbon in natural water can be composed in two fraction, particulate organic carbon (POC) and dissolve organic carbon (DOC). Normally DOC is operationally defined as passing a 0.45 μ m. (Edzward, 1993). In surface water, between 50 and 60 % of humic substances is DOC (Thurman, 1985).

2.2.2.3 UV adsorbance at wavelength 254 nm (UV- 254)

Organic compounds that are aromatic or that have conjugated double bonds absorb light in the ultraviolet (UV) wavelength region. Therefore, UV absorbance is a well known technique for measuring the presence of naturally occurring organic matter such as humic substances. However, some types of organic compounds such as simple aliphatic acids, alcohol and sugar do not absorb UV light. Moreover, pH also affects UV absorbance. If pH is increased then UV absorbance will increase (Edzward, Becker and Wattier, 1985).

Humic substrates strongly absorb ultraviolet (UV) radiation. Therefore, UV adsorption is a useful surrogate measure for NOM or precursor of THMs. The wavelength of 254 nm is the standard wavelength that minimize interference from others compounds while maximum adsorption by the interest compound. (Eaton, 1995)

The ratio between UV absorbance to TOC, referred to as specific absorbance (SUVA) ($\text{cm}^{-1}\text{mg}^{-1}\text{L}$) demonstrates a relative index of humic content (Owen et al., 1993). Specific adsorbance could suggest the nature of NOM and its consequent THM formation (Krasner et al., 1996). Higher specific adsorbance values tend to indicate higher humic content. Specific adsorbance of a humic sample depends upon the molecular weight of the substances. (Pettersson et al., 1994)

2.3 THM Precursors Removal

2.3.1 Approach for THM Precursors Removal

Researchers are working to find new methods that could control the by-products caused by current methods. Some alternatives to the complex situation of reactions are good and others produce unwanted compounds.

Rook (1979) stated that the use of macroreticular anion exchange resin followed by coagulation, sedimentation and filtration that is very effective but it is an expensive way of removing the organic precursors.

The experiment of Rook to minimize the haloform reaction by lowering the concentrations of the precursors by combination of ozone and chlorine are feasible, but they are not the most cost effective method. The study of Rook in the same year found that the removal of THMs by activated carbon breakthrough after 2-3 weeks, even though the carbon is still effective in removing larger chlorinated compounds.

Steven et al. (1976) stated that the application of granule activated carbon in the precursor removal is limited because the efficiency is only 2-3 weeks, even though the carbon is still effective in removing larger chlorinated compounds.

Olive and Lawrence (1979) demonstrated that alum treatment followed by sand filtration can removed about two-thirds of precursor. Chlorination of this treated water yields quite low haloform concentration.

The study of Young and Singer (1979) showed that the quantity of chloroform produced depends upon the total organic carbon concentration in raw water. The higher the raw water non-volatile TOC concentration, the greater chloroform formation potential. Chloroform formation decreases more than 60 percent by chlorination of the coagulated water compared with raw water. The laboratory investigation indicated that chloroform formation can be reduced by adding chlorine after pretreatment with alum.

Young and Singer (1979) also suggested that in practice, modification of the point of chlorine addition could similarly result in significant reduction in finished water concentration of chloroform. They demonstrated that chlorination following coagulation and settling is cost effective means of achieving a significant reduction in chloroform.

Potassium Permanganate can be used as a THM control. Potassium Permanganate (KMnO_4) is a very strong oxidant. It is especially effective with taste and odor problems. When added to water it turns purple, and the color changes to clear as the oxidation reaction goes to completion. There are side effects to the color characteristics. If the concentration is not carefully monitored so that the reaction goes to completion, then there could be residual color in the finished water. Sometime the KMnO_4 will react with substances differently than chlorine and control conditions that chlorine is unable to. By using KMnO_4 at the beginning of the water treatment process, you can delay the addition of chlorine till later and therefore reduce the time in which THMs can form. The KMnO_4 is known to oxidize iron and manganese, and is used to control THM precursors.

Enhanced coagulation is a hot topic of research. Researchers hope to find a solution to THM formation during disinfection processes. "Enhanced Coagulation" refers to a modification in the conventional coagulation process to gain better rates of removal of Natural Organic Matter (NOM). The enhanced coagulation process changes parameters of water treatment such as pH and coagulant dose. Because most

of the water treatment plants that exist today are working with old technology, it is hard to expect them to be able to comply with the regulations without some extra help in the treatment process. Enhanced coagulation is being tested to see how effective it is at removing particles and THM precursors. Tests are done on the raw water as well as the filtered water to measure the turbidity, TOC levels, UV-254 absorbance, and THM formation potential. Testing the characteristics of these two types of water can predict the TOC removal rate. This can forecast whether or not the changes in water treatment will help to be in compliance with the newer, stricter regulations. Many of the results depend on the raw water. Samples with higher starting TOC levels tend to have better remove rates. To ensure that the extra work being performed to remove TOC does not add more particles to the water and deteriorate the turbidity, close monitoring of the turbidity must continue.

Precursor removal by MF and UF alone is typically less than 20 percent. Scanlan et al. (1997) reported that MF without coagulant addition achieved 6.5 percent TOC removal from surface water supply in Wyoming (average raw water TOC and turbidity near 4.5 mg/L and 3.1 NTU, respectively). The UF system achieved 19 percent TOC removal. Jacangelo et al. (1995) reported that TOC removal by UF from three different surface water supplies was less than 22 percent. Memcor MF and Aquasource UF systems achieved only 11 to 12 percent TOC removal in studies at Tempe, AZ. In general, the sizes of MF and UF membranes do not reject the majority of precursors in surface water (Carollo Engineers, 2000).

Many investigators have studied the addition of powdered activated carbon (PAC) or coagulant upstream of MF or UF membranes for improved organic removal, and the results have been mixed. The addition of a modest coagulant dosage (15 to 35 ml/L alum or ferric-salt coagulant) improved TOC removal from 6.5 percent to 19 to 38 percent in studies by Scanlan et al. (1997) and Freeman et al. (1997). PAC addition (20 mg/L) upstream of MF, however, achieved only 11 percent TOC removal in one trial, and 0 percent TOC removal in another trial. Both the coagulant and PAC additions shortened the duration of water production between cleanings.

GAC can remove a significant amount of precursors (approaching 100 percent) if the EBCT is sufficient. However, as TOC is adsorbed with continued use, the carbon's adsorptive capacity becomes exhausted, and the effluent TOC concentration steadily increases. For this reason, side-stream treatment is often used for GAC contacting. GAC should also be placed in the treatment train at a location where precursor concentrations are low (such as after sedimentation or filtration). Optimization of coagulation for precursor removal prior to GAC filtration has been shown to increase the run time of the GAC by over 100 percent (Owen et al. 1998). The economics of GAC installation for precursor removal often dictate its feasibility at WTPs, because GAC is relatively expensive to be less efficient and less economical for removal of THM precursors than for removal of taste and odor control or trace organic removal.

Biologically activated carbon (BAC) prevails in systems using ozone. Ozone reacts with some organics, and makes them more biodegradable. This is a concern because it clouds lead to re-growth in the distribution system. If GAC absorbers are used following ozone application, and if the GAC contractor is not disinfected, the microbiological population will effectively remove some of the biodegradable organic carbon, as well as remove other disinfection-by-products of ozone. This biological activity also removes a portion of THM precursors: the removal is typically about 20 to 30 percent.

2.3.2 Removing of THM Precursors by Coagulation

Some of this NOM take the form of precursors for the formation of trihalomethanes via reactions with chlorine. Subsequently, these discoveries motivated several additional studies on the removal of this precursor by coagulation. While neither unique nor new, these studies provide useful operational data.

In addition to the formation of THMs and other halogenated organics during disinfection, NOM is indicative of the presence of color in the water, it utilizes adsorption capacity of activated carbon beds, exerts an oxidant demand, and may transport other contaminants via complexes through the water treatment plant. A

summary is given below of the most recent and relevant research on the chemical coagulation of NOM that is applicable to water treatment plant practice.

2.3.3 Process Variables

2.3.3.1 Coagulant Type

Aluminum and iron salts are equally capable of reducing inorganic turbidity to an acceptable level. However, they vary significantly in their ability to remove soluble NOM. Al salts are frequently found to be more effective than iron salts, but occasionally the opposite is true. Some organic, for example, have a stronger preference for iron than for aluminum. In any event, the difference in performance is not very great, and the optimum removal is usually about the same for either salt. Selection of the coagulant for NOM removal may be based on differences in chemical costs and handling requirements.

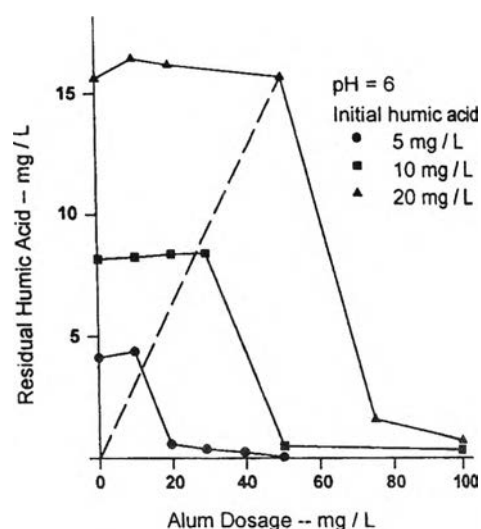
Polymerized Al and Fe chloride salts are relatively new to U.S. water treatment field, although polyaluminum chloride was first introduced about 25 years ago in Japan. Research has been conducted to compare the more traditional coagulation to these polycoagulants for removal of both turbidity and NOM. For example, it was found that polyaluminum was likely to be a better coagulant than alum for low and moderate concentrations of humic acid and clay-fulvic acid suspensions, especially at pH values <5.5 and >7.0. On the other hand, no difference was found between polymeric ironchloride over a pH range of 5-8 for the removal of NOM.

Organic, cationic polymers have received considerable investigation for the removal of NOM. In most situations, "Good" removal of humic substances and color was achieved. These polymers may be advantageous in the direct filtration of colored, low turbidity waters, but are used more often as coagulant acids in conjunction with metal salts or lime.

2.3.3.2 Coagulant Dosage

That there is a stoichiometric relation between NOM removal is seen in Figure 2.5 for the removal of color by ferric sulfate and in Figure 2.6 for the removal of humic acid by alum. In these situations, stoichiometry is defined as the require dosage begin proportional to the NOM concentration. Of course this is genetic, but it could be established for a given treatment situation. It should be noted that overdosing (exceeding the stoichiometry) may lead to restabilization of the NOM. This is possible where cationic polymers are employed as coagulation acids.

Another type of “stoichiometry” is conceivable; that is where coagulation is associated with “high” pH, “low” concentrations of NOM, and NOM that may not be of humic origin. Higher coagulant dosages are required as the [NOM] increases, but the relation is not necessarily stoichiometric. Overdosing is not possible, but any increase in NOM removal is marginal at best. This behavior is quite common for surface waters where turbidity and alkalinity are “moderate to high”. Removal of soluble synthetic organic chemicals [SOC] is expected to follow this “stoichiometry” and mechanism of coagulation.



Source : Faust and Aly, 1998

Figure 2.5 Stoichiometric relationship between alum dosage and humic acid concentration

2.3.3.3 Influence of pH

The optimum pH range of 5-6 is cited usually for removal of NOM by alum with a slightly lower value for iron salts. Data in Figure 2.6 are typical for the removal of humic and fulvic acids. This is an important operational variable, especially where coagulation is used as a pretreatment for activated carbon processes. Subsequently, the pH value would have to be adjusted upward before AC treatment and discharge into the distribution system.

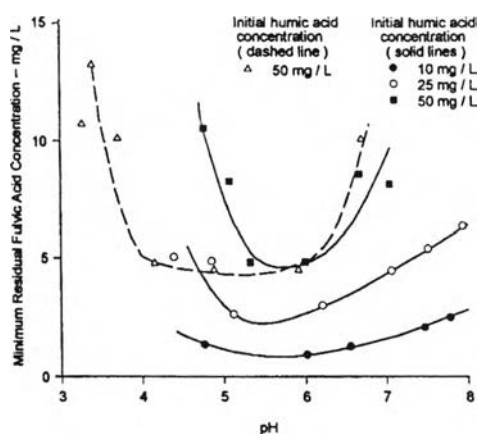


Figure 2.6 Influence of pH on the removal of fulvic acid with acid alum and humic acid with ferric chloride.

2.3.3.4 Mixing

The removal of NOM and SOCs is influenced by rapid and slow mixing. When the particulates of NOM and SOC are removed via the charge neutralization mechanism, the type of rapid mixing greatly influences this reaction; that is, it is imperative that the coagulations be dispersed into the raw water stream as rapidly as possible (<0.1 sec) so that the hydrolysis products –which develop in 0.01 to 1 sec– will destabilize the colloid. On the other hand, removal of dissolved NOM should be influenced by rapid mixing, since it will influence the charge and distribution of the metal hydrolysis products. Here it is necessary for the metal hydroxide to have a high surface area and an amorphous structure for the coprecipitation of the soluble NOM and SOCs. Aged or recycled coagulant sludges are not very effective for dissolved organic because these solids will become more crystalline as they age.

The ability of commonly used coagulants to remove TOC is discussed below:

1. *Precursor Removal by Aluminum Sulfate Coagulation.* It is well known that TOC removal by $\text{Al}_2(\text{SO}_4)_3$ coagulation is superior at solution pH values near 5.5 to 6. The TOC removal achieved within this pH range can be substantial. TOC removals of greater than 50 percent have been widely reported in the literature. Alum coagulation is also effective for DBPP removal. Cheng et al. (1995) observed approximately 30 percent THM precursor and 30 percent HAA precursor removal with 20 mg/L $\text{Al}_2(\text{SO}_4)_3$ at pH 5.5 to 6.3 for State Project and Colorado River water in Southern California.

2. *Precursor Removal by Ferric Sulfate Coagulation.* Ferric sulfate coagulation can effectively reduce TOC, THMFP, and TOXFP. In studies by Sinsabaugh et al. (1986) a 20 mg/L $\text{Fe}_2(\text{SO}_4)_3$ dosage removed nearly half of the THMFP and the TOXFP. Increasing the dosage to 50 mg/L $\text{Fe}_2(\text{SO}_4)_3$ increased these removals to approximately 70 percent. The pH during coagulation was maintained near 5.0.

3. *Precursor Removal by Ferric Chloride Coagulation.* Ferric chloride is also very effective for NOM removal. Dryfuse et al. (1995) optimized TOC removal using bench-scale FeCl_3 coagulation for three different source waters. The percentage DOC removal ranged from 46 to 71 percent, and the removal of THMFP and HAAFP was slightly greater, ranging from 59 to 90 percent. Ferric chloride coagulation was found to preferentially remove the high molecular weight, humic fraction of organics; non-humics were also removed by FeCl_3 coagulation, but to a lesser extent. The differences between iron and aluminum-salt coagulants include the optimum pH values for organics removal, solubilities, surface areas, and surface charge. A number

of studies comparing alum to iron-based coagulants have found that iron achieved greater precursor removal than alum (e.g. Vilage et al., 1997 ; Shorney et al., 1998)

4. *Precursor Removal by Polyaluminum Chloride Coagulation.*

Polyaluminum chloride is a partially hydrolyzed metal coagulant prepared by adding a base to the coagulant to 'pre-form' the polymeric aluminum species that may be more effective in achieving organics removal. Dempsey et al. (1984) reported that PACl outperformed $\text{Al}_2(\text{SO}_4)_3$ for fulvic acid removal. The PACl coagulant was better at all pH values above and below those for optimum alum coagulation.

2.4 COAGULANTS

The most widely used coagulants in water treatment are aluminium and iron salts. Aluminium salts are employed more frequently than iron salts because they are usually cheaper. Iron salts have an advantage over aluminium salts because they are effective over a wider pH range. The principle factors affecting the coagulation and flocculation of water or wastewater are turbidity; suspended solids; temperature; pH; cationic and anionic compositions and concentrations; duration and degree of agitation during coagulation and flocculation; dosage and nature of the coagulant; and, if required, the coagulant aid. The selection of a coagulant requires the use of laboratory or pilot plant coagulation studies, since a given water or wastewater may show optimum coagulation results for a particular coagulant. Usually, laboratory studies using the jar test are adequate for selecting a coagulant for a water treatment plant, whereas laboratory and frequently pilot studies are required for wastewater.

2.4.1 Polyaluminium chloride (PACl)

PACl is a coagulant developed in Japan. It has been used in Asia, Australia and Europe for water treatment since the late 1960's and rapidly expanding into commercial in mid 1980's. PACl is a coagulant that consists of partially hydrolyzed aluminium chloride (AlCl_3) produced by the addition of base to

concentrated AlCl_3 solution under specified conditions. The general formula of PACl may be expressed as;



The simplest polyaluminium form is shown in Figure 2.7, the dimer has two octahedrally coordinated aluminium ions joined together by two shared hydroxyl groups that displaced four water molecules.

PACl can be prepared by mixing a hot aqueous solution of AlCl_3 with a small amount of a solution or suspension of aluminium hydroxide, which in turn can be obtained by precipitation of a solution of AlCl_3 or sulfate by sodium carbonate. The composition of PACl will depend on the concentration of the stock AlCl_3 solution, degree of neutralization (r), type of base, mixing technique, presence of sulfate, temperature, pressure, and on occasion, age of the solution. PACl is supplied as a liquid with the equivalent of 10% AlCl_3 . Dilute solution of concentration 4-3% show evidence of slow hydrolysis.

2.4.2 Theory of the Action of PACl

Different reactions may occur when PACl is added to polluted water, depending upon the impurities in the water. The aluminium species can act both as coagulants (destabilizing agents) in stable colloid suspensions and as precipitants of soluble contaminants. According to Stumm and O'Melia (1968), PACl can function as a coagulant for the destabilization of colloid and particle mainly in two ways:

- 1) Positively charged aluminium polymers adsorb onto the negatively charged particles, neutralizing their charge and permitting effective aggregation when sufficient contact opportunities are provided. This process works well for concentrated suspensions where flocculation is fast and at pH levels where cationic polymers are formed rapidly (pH \approx 5-6). Increasing concentration of organic matter require increasing amounts of destabilization chemical for charge neutralization by adsorption; stoichiometry is observed.

2) $\text{Al}(\text{OH})_3$ (s) can be precipitated before charge neutralization occurs. This will typically happen in low organic matter water at $\text{pH} > 5-6$. The colloidal matter is removed as a consequence of entrapment to the "stick" hydroxide precipitate, the "sweep floc". Increasing concentration of colloidal matter requires fewer contact opportunities, so that coagulant requirement can even decrease slightly with increasing colloidal concentration; stoichiometry is not observed.

2.4.3 Advantages of PACl

Many researchers indicated that PACl coagulants have several advantages over the tradition metal salt coagulants in most waters, which can be summarized as follow:

- Better overall purification efficiency.
- Better floc separation.
- Wider working pH range.
- Less sensitive to low temperatures.
- Lower residual aluminium concentration.

In addition, there are effects that normally are favorable, such as lower alkalinity consumption resulting in less pH drop when added to the water. The following are briefly discussing these effects based on references from the literature both on drinking water and wastewater treatment.

1) Improved Overall Purification Efficiency

PACl are used extensively in the treatment of turbid waters for drinking water preparation. The development of these coagulants in the Sweden and Canada show that PACl seems to give lower residual turbidity values than alum at a given dosage, corresponding to lower Al dosage in order to obtain the same treatment result.

Most of reports on turbidity removal also conclude that the removal of organic matter was improved. In addition there are several reports where specifically soft, humic waters have been treated, demonstrating that a PACl gave better color removal efficiency at equivalent Al doses and PACl gave better color removal than aluminium sulfate.

For wastewater treatment, several studies reports have shown PACl to give better result than aluminium sulfate with respect to particle separation. Hass et al. (1984) found, however, that phosphate removal was poorer the higher the basicity of the coagulant.

2) Better Floc Separation Effect

Several authors have found that PACl have given flocs with improved floc separability, with respect to settleability, filtrability and sludge dewaterability.

Hass et al. (1984) found better settling rates in wastewater coagulation with PACl than with alum. The higher the basicity, however, the lower was the settling rate. These authors also studied the dewaterability of the sludge. It is difficult to draw absolute conclusion from their work, but their result seem to indicate a higher specific resistance for the PACl coagulated sludge than for that coagulated by alum.

In coagulation / direct filtration experiments of a humic water, Fettig et al. (1988) reported that one could achieve a higher net water production with PACl than with alum as a consequence of the higher optimum filter velocity that could be achieved with the PACl.

3) Wider Working pH Range

Invariably, it seems that the pH range which coagulation is successful is considerably wider with PACl than with alum coagulation. This was the case in turbidity removal, inhumic substance removal and in wastewater treatment.

Dentel (1988) hypothesizes that the advantage of PACl at the pH extremes stems from the circumvention of solubility limitations. In other words, the positively charged insoluble aluminium hydroxide species, which act as destabilization agents, are preformed and do not depend on pH conditions within the water to be treated.

4) Less Sensitive to Low Temperatures

It is well known that the performance of coagulation plants deteriorates at very low temperatures due to an efficiency loss in all the treatment steps (coagulation, flocculation, settling and filtration). Several authors have reported that PACl is more efficient at low temperatures than the basic metal salts.

5) Lower Residual Al concentration

Simpson (1996) demonstrated that in all three full-scale drinking water plants, the residual Al concentration was lower with the use of PACl than with alum at equivalent dosages. This is relevant in the discussion about aluminum having an influence on the occurrence of Alzheimer disease.