



## Chapter II

### Literature Review

#### 2.1 Atmospheric Dispersion

Atmospheric dispersion of pollutant is a dilution process which the surrounding air is replaced by the pollutant. For example, whereas surrounding air is generally transported by wind velocity. If the pollutant folded into this air mass is advected together with it. A pollutant free air mass will then move to replace. Although molecules are diffusing in the atmosphere, the molecular diffusion in the atmosphere is usually negligible compared to the atmospheric diffusion of parcels of air. Thus, the atmospheric pollutant dispersion process is the diffusion process resulting from turbulent eddies and wind direction variation.

Fick (1855), a German physiologist, proposed the first model for analysis of diffusion. The variations of his basic idea have been called Fickian diffusion, transfer theory, and K theory. The fundamental notion is that the time change in contaminant concentration at a point results from the existence of a gradient of concentration at that point, and that the diffusion behavior of the medium may be characterized by its diffusivity,  $K_d$ . Thus

$$\frac{dC}{dt} = K_d \nabla^2 C \quad (2.1)$$

where

$C$  = concentration of the non-gaseous pollutant; ( $g/m^3$ )

$t$  = time; (s)

$K_d$  = diffusion coefficient; ( $m^2/s$ )

For steady state, with a steady emission rate  $Q$ , a steady wind of uniform speed  $\bar{u}$ , and with limited anisotropy, ( $K_x \neq K_y \neq K_z$ ), the plume of pollutant will expand by diffusion downwind of the source and Equation (2.1) takes the form as follows:

$$\bar{u} \left( \frac{\partial C}{\partial x} \right) = K_x \left( \frac{\partial^2 C}{\partial x^2} \right) + K_y \left( \frac{\partial^2 C}{\partial y^2} \right) + K_z \left( \frac{\partial^2 C}{\partial z^2} \right) \quad (2.2)$$

Solutions to Equation (2.2) have been formulated by Roberts (1923)

$$C(x,y,z) = \left\{ \frac{Q}{4\pi x K_y^{0.5} K_z^{0.5}} \right\} \exp \left[ -\frac{\bar{u}}{4x} \left( \frac{y^2}{K_y} + \frac{z^2}{K_z} \right) \right] \quad (2.3)$$

with the following boundary conditions

- a)  $C \rightarrow \infty$  as  $x \rightarrow 0$  infinite  $C$  at source
- b)  $C \rightarrow 0$  as  $x,y,z \rightarrow \infty$  zero  $C$  at great distance
- c)  $K_z \left( \frac{\partial C}{\partial z} \right) \rightarrow 0$  as  $z \rightarrow 0$  no downward transport into the earth
- d)  $\int_0^\infty \int_{-\infty}^\infty \bar{u} C(x,y,z) \delta_y \delta_z = Q, x > 0$  the rate of transport of contaminant through any vertical plane downwind is constant and equals the emission rate at the source  $Q$

where

- $x$  = distance downwind from the source; (m)
- $y$  = distance horizontally from the plume center line; (m)
- $z$  = distance vertically from the plume center line; (m)
- $K_x$  = diffusion coefficient in  $x$  direction; ( $m^2/s$ )
- $K_y$  = diffusion coefficient in  $y$  direction; ( $m^2/s$ )
- $K_z$  = diffusion coefficient in  $z$  direction; ( $m^2/s$ )

Sutton (1932) modified Equation (2.3) describing atmospheric dispersion and evaluation through field studies of parameters related to dispersion for the continuous point source. Later, Pasquill and Gifford (1961) developed Sutton's equation to be the Gaussian plume model which is at present widely used.

## **2.2 Mathematical Models of Air Pollution Simulations**

Mathematical models to represent the diffusion mechanism have flexibility and versatility to evaluate the atmospheric concentrations for changing meteorological and pollutant sourcing conditions. Presently available mathematical models, however, have application limits and difficulties in applying them for special diffusion problems involving complex terrain, buildings, and meteorological conditions. Therefore, we have to select proper models each time depending on the nature of the problem e.g. a mathematical model for a long term diffusion problem or a fluid model for a terrain affected diffusion. (JICA, 1990)

Mathematical models of air pollution simulations are classified into 2 types as follows:

### **2.2.1. Analytical models**

### **2.2.2. Numerical models**

#### **2.2.1 Analytical Models**

An analytical model is one in which an analytical solution to the diffusion equation is used to estimate concentration of pollutants. Many solutions have been proposed for different boundary and flow conditions. Among them, the Gaussian plume model is most commonly in use.

### • Gaussian Plume Model

The Gaussian plume model is the solution of the Fickian type diffusion equation in which pollutants are emitted continuously at a constant flow rate. Then the pollutant disperses as shown in Figure 2.1 by a plume and in concentration whose lateral and vertical profiles are expressed by the Gaussian distributions. (JICA, 1990)

The concentration of the pollutant of Gaussian plume model at a point (x,y,z) for elevated point source is given by

$$C(x,y,z) = \left( \frac{Q}{2\pi\sigma_y\sigma_z\bar{u}} \right) \exp\left[ -\frac{1}{2} \left( \frac{y}{\sigma_y} \right)^2 \right] \left\{ \exp\left[ -\frac{1}{2} \left( \frac{z-H}{\sigma_z} \right)^2 \right] + \exp\left[ -\frac{1}{2} \left( \frac{z+H}{\sigma_z} \right)^2 \right] \right\} \quad (2.4)$$

where

$C(x,y,z)$  = non-gaseous concentration downwind from the source at position x,y,z; (g/m<sup>3</sup>)

$Q$  = sulfur dioxide emission rate; (g/s)

$\bar{u}$  = average wind velocity; (m/s)

$x$  = distance downwind from the source; (m)

$y$  = distance horizontally from the plume center line; (m)

$z$  = distance vertically from the plume center line; (m)

$H$  = effective height; (m)

$\sigma_y, \sigma_z$  = horizontal and vertical dispersion coefficients, respectively; (m)

Equation (2.4) is based upon several assumptions, including:

a) No initial concentration or no plume history.

b) Steady-state conditions - ideal gas, continuous uniform emission rate,

homogeneous horizontal wind field, representative mean wind velocity, no directional wind shear in the vertical, infinite plume.

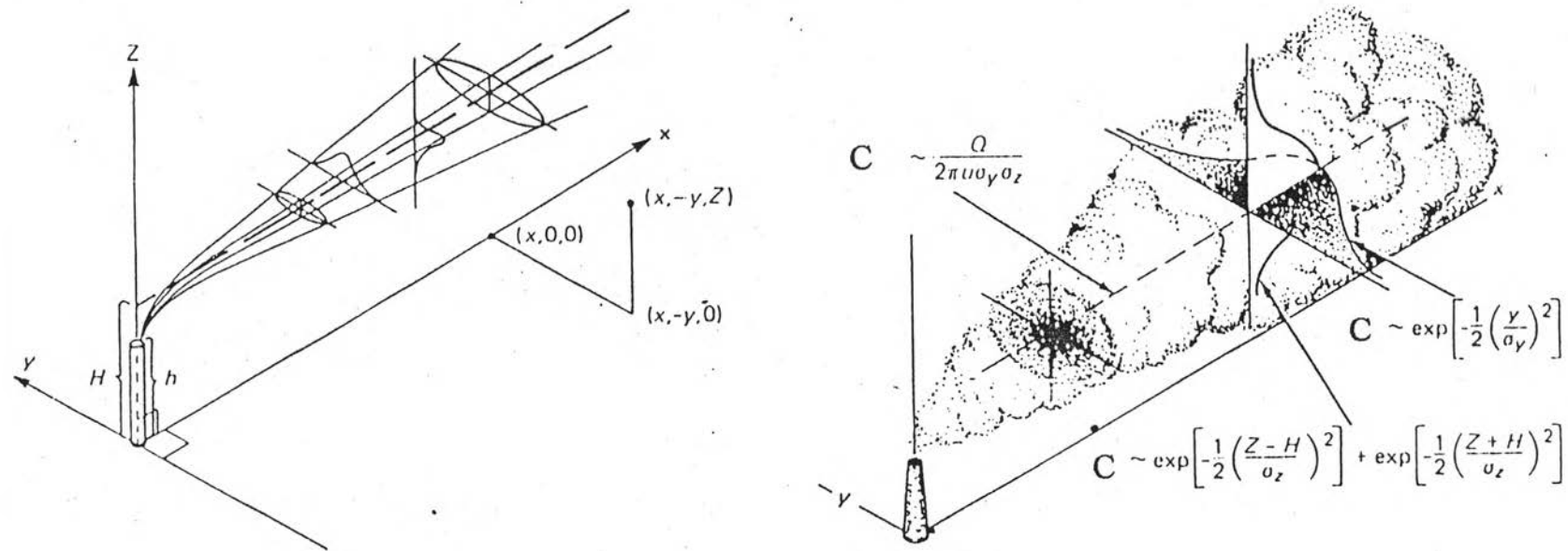


Figure 2.1 Three-Dimensional Concentration Profiles of Gaussian Plume Model (Turner, 1970)

- c) Total reflection of the plume takes place at the earth's surface.
- d) Gaussian distribution - the pollutant material within the plume takes on a Gaussian distribution in both the horizontal crosswind and vertical direction.
- e) No downwind diffusion.
- f) No inversion layer.
- g) The pollutant emitted is a stable gas or aerosol which remains suspended in the air and participates in the turbulent movement of the atmosphere, none of the material is removed as the plume advects and diffuses downwind.

The dispersion coefficients,  $\sigma_y$  and  $\sigma_z$ , in Equation (2.4) can be defined according to atmospheric stability class and downwind distance. The popular dispersion coefficients are Pasquill-Gifford and ASME dispersion coefficients as depicted in Figure 2.2 and 2.3, respectively. The atmospheric stability class can be classified in accordance with the wind velocity and incoming solar radiation for day or cloud cover for night as shown in Table 2.1.

**Table 2.1 Pasquill Chart for Determining Atmospheric Stability Class (Turner, 1970)**

Surface wind speed (at 10 m), m/s	Day			Night	
	Incoming solar radiation			Thinly overcast or 4/8 low cloud	3/8 cloud
	Strong	Moderate	Slight		
<2	A	A-B	B		
2-3	A-B	B	C	E	F
3-5	B	B-C	C	D	E
5-6	C	C-D	D	D	D
>6	C	D	D	D	D

Neutral class D should be assumed for overcast conditions during day or night.

Stability class	Class description
A	Extremely unstable
B	Unstable
C	Slightly unstable
D	Neutral
E	Slightly stable
F	Stable to extremely stable

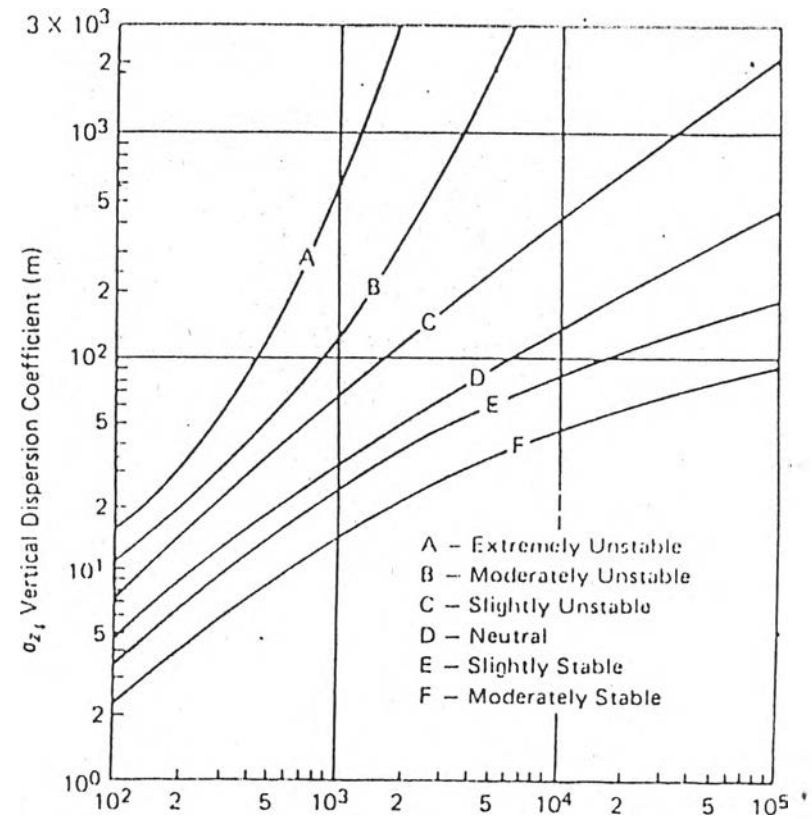
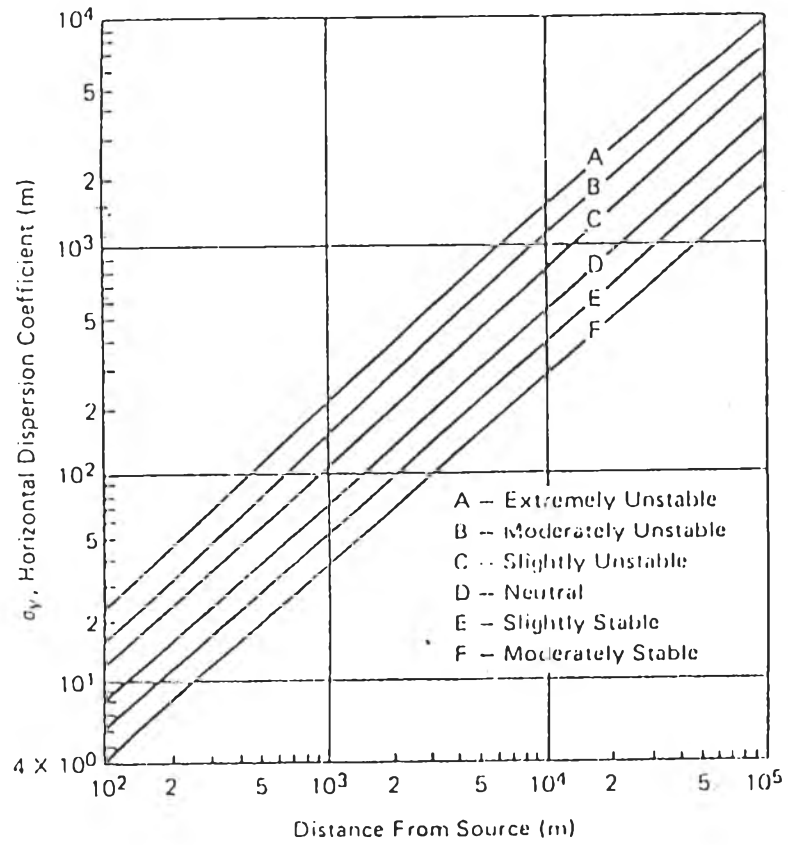


Figure 2.2 Pasquill-Gifford Dispersion Coefficients (Slade, 1968)

a)  $\sigma_y$ , horizontal dispersion coefficient

b)  $\sigma_z$ , vertical dispersion coefficient

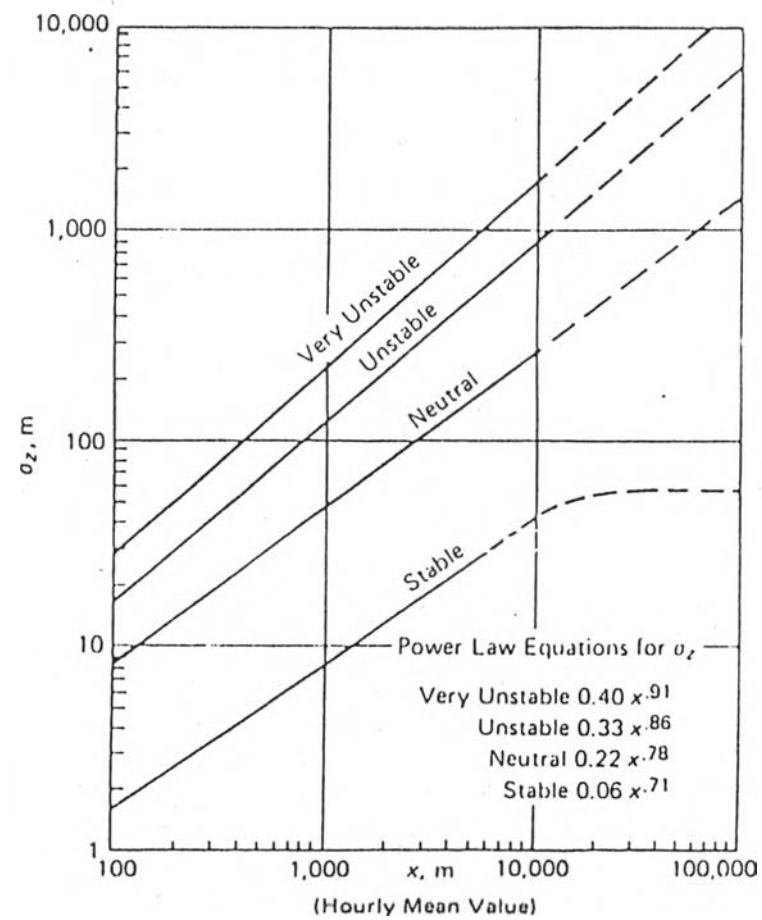
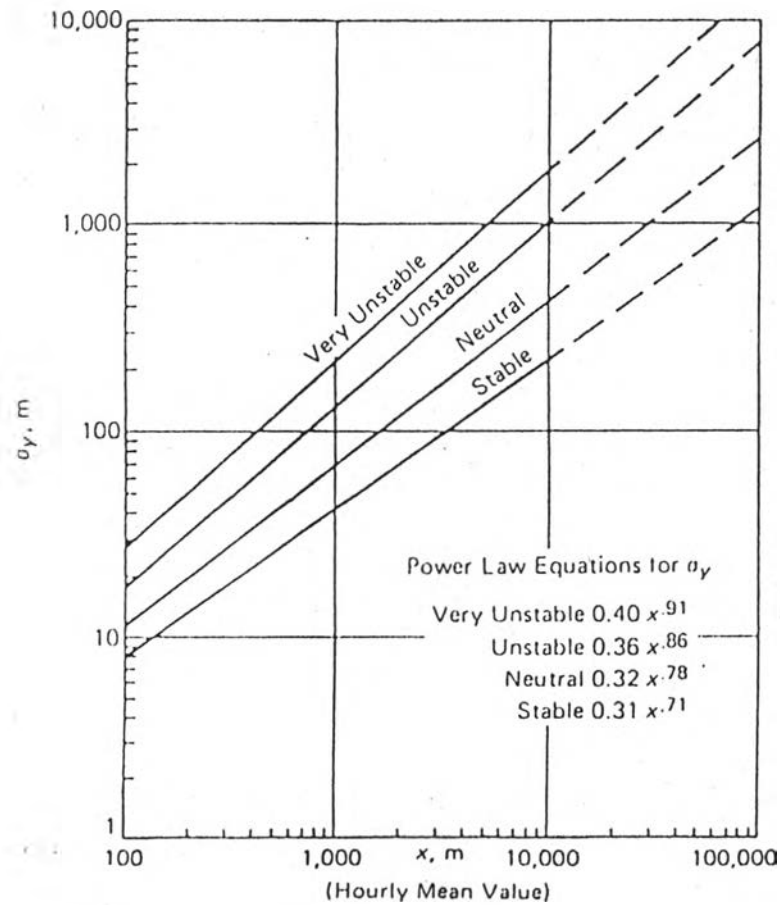


Figure 2.3 ASME Dispersion Coefficients (Smith, 1968)

a)  $\sigma_y$ , horizontal dispersion coefficient

b)  $\sigma_z$ , vertical dispersion coefficient



### 2.2.2 Numerical Models

Numerical models solve the diffusion equation such as Equation (2.1) and (2.2) by the finite difference method or the finite element method using a computer. They are thought effective for unstable conditions and also for complex meteorological conditions. But they often require long computation time and expenses. It is not recommended for use in the prediction of average concentration under changing meteorological conditions that incur considerable expense. In accordance, numerical methods are thought suitable for roadway diffusion problems to which analytical models can not be applied or for diffusion of chemically active pollutants such as hydrocarbon and oxidants. (JICA, 1990)

- **Numerical Models Simulated by the Monte Carlo Method**

The Monte Carlo method also known as the Markov Chain or the random walk method is one of the most popular in modeling dispersion. Ley (1982) mentioned that to model the dispersion of emissions of pollutant into the atmosphere and to predict the resulting concentration profiles, discrete step random walk techniques simulating numerical particle motion were simple to apply and produced accurate results quickly and efficiently. They were applicable to a large number of situations where it was either not possible to find an analytic solution or else not practical to apply such a solution because of its complexity. Due to its advantages as stated above, Patterson et al. (1981) and Panich (1983) used the Monte Carlo method to solve the mathematical model of atmospheric pollutant dispersion. Consequently, this method can closely model the diffusion and chemical processes.

The EPA model by Patterson et al. (1981) used the Monte Carlo method in simulating transport of the pollutants. They represented the mass of sulfur dioxide as

204 quanta, and advected these quanta in horizontal flow in well-mixed vertical layers (at the time, only one vertical layer). Diffusion is basically K theory-type, with K set to be  $100,000 \text{ m}^2/\text{s}$ . Advection is computed using trajectories estimated by the method of Heffter et al. (1975). This model was validated using SURE data for sulfate concentrations in the eastern United States in August 1977. The model's results showed spatial and temporal agreement with observation throughout the month, with a correlation of daily average sulfate concentrations (model VS measured) of 0.63. This model, however, lacked realistic meteorological input such as multiple vertical layers and transport above the mixing height. Moreover the chemistry was constant throughout day and night (the first order) which was not true for photochemical and heterogeneous oxidation mechanisms. Because of the lack of models that had quality meteorological input and chemical input, Panich (1983) developed a mathematical model in the relationships between meteorology, chemistry and aerosol dynamics.

Panich (1983) developed a mathematical model for determining the effect of sulfur dioxide emissions on visibility reduction in the eastern United States. It consisted of transport, chemical reaction models, aerosol dynamics, and light scattering calculations, which were used simultaneously to determine the visibility-reducing property of the resulting atmospheric aerosols.

The transport model was a three-dimensional Monte Carlo system simulating multiple Gaussian plumes on a  $14 \times 14 \times 5$  grid. Grid size was  $160 \text{ km} \times 160 \text{ km} \times 300 \text{ m}$ , and was flexible. Wind speed, direction, atmospheric stability coefficients and mixing height at each grid point were used to calculate the movement of  $\text{SO}_2$  and sulfate particles along the trajectories. Deposition and chemical reactions change or remove pollutants. In the chemical portion of the model, there were additional algorithms that determined the extent of sulfur dioxide oxidation above and below the

mixing layer. In the aerosol dynamics portion, the resulting light extinction coefficient at the receptor sites was calculated.

The results from a number of runs of the model showed that diurnal mixing height variations strongly affected the conversion rate of sulfur dioxide to sulfate in the mixed layer for first order oxidation reaction. For tall stacks, sulfur dioxide could be transported with little or no deposition to the ground if the plume was above the mixed layer, or was within a very deep mixed layer (i.e. during the afternoon).

Case studies of episodes of high sulfate concentrations that occurred during August 1976 and 1977 showed that the model was capable of realistically simulating visibility reduction due to multiple sulfur dioxide sources in the eastern United States. Certain meteorological factors such as the location of the prevailing high pressure system, have been identified as the major reasons why episodes occurred on some days but not on others. The results also indicated that the sulfate aerosols observed in the northeastern United States were caused by the sulfur emitted both locally and from sources outside the region, but the high sulfate concentrations during the episodes were always the result of long-range transport of sulfate. (Panich, 1983)

## 2.3 Sulfur Dioxide

Sulfur forms a number of oxides such as SO, SO<sub>2</sub>, S<sub>2</sub>O<sub>3</sub>, SO<sub>3</sub> and S<sub>2</sub>O<sub>7</sub> but only sulfur dioxide (SO<sub>2</sub>) and sulfur trioxide (SO<sub>3</sub>) are of any importance as gaseous air pollutants. (Stern, 1976)

### 2.3.1 Sources of Sulfur Dioxide

The sources of sulfur dioxide are combustion of fossil fuels, volcanoes, decomposition and combustion of organic matter. (Seinfeld, 1975)

### 2.3.2 Properties of Sulfur Dioxide

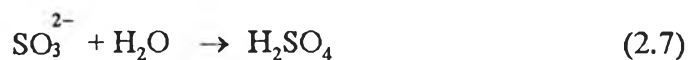
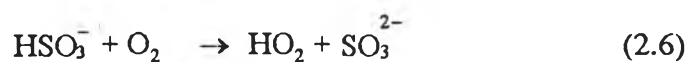
Sulfur dioxide is a colorless gas with a pungent, irritating odor. Most people can detect it by taste at 0.3 to 1 ppm (780 to 2620  $\mu\text{g}/\text{m}^3$ ). It is highly soluble in water: 11.3 gm/100 ml as compared to 0.169 gm/100 ml for carbon dioxide, forming weakly acidic sulfurous acid ( $\text{H}_2\text{SO}_3$ ). (Stern, 1976)

## 2.4 Atmospheric Oxidation of Sulfur Dioxide

The oxidation of sulfur dioxide to sulfate aerosols in the atmosphere may occur by photochemical reactions in the gas-phase or by heterogeneous reactions in the liquid-phase.

### 2.4.1 Photochemical Reactions in the Gas-Phase

The most important chemical pathways of gas-phase oxidation of sulfur dioxide in the atmosphere involve the reaction of sulfur dioxide with OH,  $\text{CH}_3\text{O}_2$  and  $\text{HO}_2$  radicals. (Seigneur et al., 1982) But the reaction with OH is the most significant gas-phase oxidation pathway for sulfur dioxide and the steps of reactions are as below. (Calvert et al., 1978 and Calvert and Stockwell, 1983)



Alkezweeny and Powell (1977) estimated the transformation rate of sulfur dioxide to sulfate from data collected by aircraft following a tetroon northeast of St. Louis, Missouri, on 10 and 11 August 1975. Assuming deposition velocities of 1 cm/s and 0.1 cm/s for sulfur dioxide and sulfate, respectively, the analysis including 90%

confidence limits, yielded a rate of  $0.14 \pm 0.04$  per hour for the first day, and  $0.1 \pm 0.02$  per hour for the second. The confidence limits did not preclude the likelihood that the rate was the same for both days, in which case it would have been 0.1-0.12 per hour.

## 2.4.2 Heterogeneous Reactions in the Liquid-Phase

The liquid-phase oxidations of sulfur dioxide include oxidation by  $O_2$ ,  $O_3$ ,  $H_2O_2$  and  $O_2$  catalyzed by transition metal ions such as  $Fe^{3+}$  and  $Mn^{2+}$ . (Seigneur et al., 1982) Because there are the complexities and dispersion limitations of oxidants ( $O_3$  and  $H_2O_2$ ) in plume and the ozone concentration is not so high in Bangkok and Samut Prakarn. So in this research, the heterogeneous reactions of sulfur dioxide with oxidants are negligible and the liquid-phase oxidation of sulfur dioxide by  $O_2$  catalyzed by transition metal ions is interested and reviewed in the subsequent sections.

### 2.4.2.1 Mechanisms of the Catalytic Oxidation of Sulfur Dioxide in the Liquid-Phase

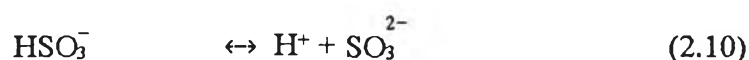
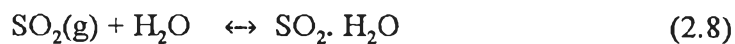
The individual steps in the liquid-phase catalytic oxidation of sulfur dioxide are (Seinfeld, 1975):

- a) Gas-phase diffusion of sulfur dioxide to the drop.
- b) Diffusion of sulfur dioxide from the drop surface to the interior.
- c) Catalytic reaction in the interior.

At steady-state conditions, the overall rate of sulfur dioxide conversion is limited by the catalytic reaction step.

### 2.4.2.2 Absorption Equilibria of Sulfur Dioxide in Water

Absorption of sulfur dioxide in water results in (Seinfeld, 1980)



with

$$K_1 = [\text{SO}_2 \cdot \text{H}_2\text{O}] / P_{\text{SO}_2}$$

$$K_2 = [\text{H}^+][\text{HSO}_3^-] / [\text{SO}_2 \cdot \text{H}_2\text{O}]$$

$$K_3 = [\text{H}^+][\text{SO}_3^{2-}] / [\text{HSO}_3^-]$$

In the system of  $\text{SO}_2$  and water,

$$[\text{H}^+] = [\text{OH}^-] + [\text{HSO}_3^-] + 2[\text{SO}_3^{2-}] \quad (2.11)$$

or expressing each concentration in terms of  $[\text{H}^+]$ ,

$$[\text{H}^+]^3 - (K_w + K_1 K_2 P_{\text{SO}_2}) [\text{H}^+] - 2K_1 K_2 K_3 P_{\text{SO}_2} = 0 \quad (2.12)$$

The total unoxidized sulfur in solution is often referred to as S(IV), i.e.

$$[\text{S(IV)}] = [\text{SO}_2 \cdot \text{H}_2\text{O}] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}] \quad (2.13)$$

which is related to  $P_{\text{SO}_2}$  and  $[\text{H}^+]$  by

$$[\text{S(IV)}] = K_1 P_{\text{SO}_2} \left[ 1 + \frac{K_2}{[\text{H}^+]} + \frac{K_2 K_3}{[\text{H}^+]^2} \right] \quad (2.14)$$

### 2.4.2.3 Liquid-Phase Oxidation of Sulfur Dioxide by O<sub>2</sub> Catalyzed by Transition Metal Ions

Brimblecombe and Spedding (1974) established the rate of oxidation of low concentrations of sulfur dioxide (about 10<sup>-5</sup> M) in aqueous solutions containing traces of Fe(III) (about 10<sup>-6</sup> M) as these concentrations approach those which might be expected in the atmospheric aerosol. The results obtained showed that Fe(III) acted as a catalyst and increased the rate of oxidation. The reaction was the first order kinetic with respect to S(IV) concentrations and written in the form as follows:

$$\frac{-d[S(IV)]}{dt} = K[Fe(III)][S(IV)] \quad (2.15)$$

$K = 100 \text{ l.mole}^{-1}.\text{s}^{-1}$  at 20 °C and pH 4.9

Freiberg (1974) studied effects of relative humidity and temperature on iron-catalyzed oxidation of sulfur dioxide in atmospheric aerosols and its subsequent neutralization by ambient ammonia. The results were concluded that the oxidation rate increased rapidly with increasing relative humidity (particularly at high relative humidities) and it decreased by about an order of magnitude for an increment of 5 °C in temperature. Freiberg (1974)'s reaction rate was written as the following relationship.

$$\frac{-d[SO_2]}{dt} = K_o \beta_s^2 K_s^2 \frac{[\beta_n K_n \lambda_z]^3}{[2(1-RH)K_w]} [SO_2]^2 [Fe^{3+}] [NH_3]^3 \quad (2.16)$$

where

$K_o$  = rate constant of the reaction; (m<sup>3</sup>/mole-min)

$\beta_s$  = Ostwald's constant for sulfur dioxide

$K_s$  = first dissociation constant of sulfurous acid; (mole/m<sup>3</sup>)

$\beta_n$  = Ostwald's constant for ammonia

$K_n$  = dissociation constant of ammonia; (mole/m<sup>3</sup>)

$\lambda_z$  = pressure-lowering coefficient for ammonium sulfate; (m<sup>3</sup>/mole)

RH = relative humidity

$K_w$  = dissociation constant of water; (mole/m<sup>3</sup>)<sup>2</sup>

t = time (min)

[SO<sub>2</sub>] = concentration of sulfur dioxide; (mole/m<sup>3</sup>)

[Fe<sup>3+</sup>] = concentration of iron; (mole/m<sup>3</sup>)

[NH<sub>3</sub>] = concentration of ammonia; (mole/m<sup>3</sup>)

The factor  $K_o * \beta_s^2 * K_s^2 * \beta_n^3 * K_n^3 / K_w$  from Equation (2.16) contained the dependence on temperature and was concluded in Table 2. 2.

Table 2.2 Effect of Temperature on the Value of  $K_o * \beta_s^2 * K_s^2 * \beta_n^3 * K_n^3 / K_w$

(Freiberg, 1974)

T (°C)	$K_o * \beta_s^2 * K_s^2 * \beta_n^3 * K_n^3 / [K_w * 10^{-35}]$ (m <sup>6</sup> /mole <sup>2</sup> -min)
5	2349.743
10	269.813
15	29.130
20	3.501
25	0.559
30	0.075

Freiberg (1978) developed the oxidation of sulfur dioxide to sulfate model in expanding plumes for three oxidation reactions: a first order direct homogeneous oxidation, a heterogeneous catalytic oxidation and a second order homogeneous oxidation. The model predicted that for all oxidation reactions except the first order direct homogeneous, the conversion proceeded to a fractional asymptotic limit. The



values of the fractional asymptotic limit as well as the values of the half lives of reaction depended on the ratios of the 'chemical' parameters to the 'dispersion' parameters.

Aqueous phase oxidation of sulfur dioxide or S(IV) by H<sub>2</sub>O<sub>2</sub>-metal ions at a H<sub>2</sub>O<sub>2</sub> concentration much lower than S(IV) was studied by Ibusuki et al. (1990). Of the metal ions, Fe<sup>2+</sup> showed the highest catalytic activity, i.e. the oxidation of S(IV) continued after most of the H<sub>2</sub>O<sub>2</sub> was consumed. The dependence of the rate on the concentration of S(IV), H<sub>2</sub>O<sub>2</sub>, Fe<sup>2+</sup> or H<sup>+</sup> and temperature was determined. The following rate expression and low apparent activation energy of 40.7 KJmole<sup>-1</sup> were evaluated:

$$\frac{-d[S(IV)]}{dt} = 620[S(IV)]^2[Fe^{2+}]^{0.5}[H^+]^{-0.5} \quad (2.17)$$

Catalytic effects of metal ions such Fe(III) and Mn(II) on the oxidation of S(IV) in aqueous solution at concentrations of metal ions and S(IV) as found in an urban atmosphere were studied by Grgic et al.(1991). The following rate expressions were obtained:

$$-r_{S(IV)} = K[Fe(III)][S(IV)] \quad (2.18)$$

$$-r_{S(IV)} = K[Mn(II)][S(IV)]^{0.65} \quad (2.19)$$

The activation energy were 104 KJmole<sup>-1</sup> for Fe(III) and 63.3 KJmole<sup>-1</sup> for Mn(II).

Barrie and Georgii (1976) first pointed out the possibility of a catalytic synergism between Mn(II) and Fe(II) or Fe(III), i.e. the rate of S(IV) oxidation for an equimolar mixture of Mn(II) and iron was an order of magnitude greater than that obtained for Mn(II) alone.

The reaction kinetics of sulfur dioxide oxidation by oxygen catalyzed by mixtures of Mn(II) and Fe(III) in aqueous solutions over a wide range of pH from 2.6 to 6.5 have been studied at low concentrations of S(IV) and the metal ions by Ibusuki and Takeuchi (1987). The catalytic synergism between the two catalysts as a function of [Mn(II)].[Fe(III)] has been confirmed. The following rate expression was obtained with a rate constant of  $K_s = (3.6 \pm 0.6) \times 10^{10} \text{ l.mole.s}^{-1}$  at a pH of 4.2 and a temperature of 23.8 °C.

$$\frac{-d[\text{S(IV)}]}{dt} = K_s[\text{Mn(II)}][\text{Fe(III)}][\text{S(IV)}] \quad (2.20)$$

Martin and Good (1991) found that at concentrations of S(IV) of  $10^{-5} \text{ mole.l}^{-1}$  and lower, there was a synergism between Fe(III) and Mn(II) catalysis of the autoxidation. This synergism had a different rate law from the synergism seen at higher concentrations of sulfur. At pH 3.0, the rate law was written in the form as follows:

$$\frac{-d[\text{S(IV)}]}{[\text{S(IV)}]dt} = K_1[\text{Fe(III)}] + K_2[\text{Mn(II)}] + K_3[\text{Mn(II)}][\text{Fe(III)}] \quad (2.21)$$

where  $K_1 = 2600 \text{ M}^{-1}\text{s}^{-1}$ ,  $K_2 = 750 \text{ M}^{-1}\text{s}^{-1}$  and  $K_3 = 1.0 \times 10^{10} \text{ M}^{-2}\text{s}^{-1}$ . A similar relation was found at pH 5.0. It was estimated that this effect raised the catalyzed oxidation rate of sulfur in clouds several times over the iron rate taken separately, for typical atmospheric concentrations of iron, sulfur and manganese.

## 2.5. Potential Role of Ammonia on the Atmospheric Oxidation of Sulfur Dioxide in the Liquid-Phase

Atmospheric ammonia is classified into 2 parts by Saxena et al. (1986)

a) Ammonia-rich environment. This case is defined by  $[\text{NH}_3] > 2[\text{H}_2\text{SO}_4]$  where  $[\ ]$  denotes molar concentration of the component.

b) Ammonia-deficient environment. This case is defined by  $[\text{NH}_3] \leq 2[\text{H}_2\text{SO}_4]$  where  $[\ ]$  denotes molar concentration of the component.

The potential role of ammonia on the atmospheric oxidation of sulfur dioxide in the liquid-phase is reviewed as follows.

The kinetics of the conversion of ammonia and sulfur dioxide to ammonium sulfate in water droplets in the atmosphere in the absence of metal ion catalysts has been reconsidered by McKay (1971). It was concluded that the reaction was an order of magnitude faster than earlier work suggested, and that lowering the temperature increased the rate by a large factor. In a cloud or a thick mist appreciable amounts of ammonium sulfate may be formed in a few minutes; nevertheless a substantial proportion of unreacted ammonia may sometimes persist for hours, even though excess sulfur dioxide is present and the initial reaction is fast.

By studying the buffering effect of atmospheric ammonia on sulfur dioxide oxidation, Freiberg (1974) defined the relationship between hydrogen ion and ammonia concentrations as shown below.

$$[\text{H}^+] = \frac{2(1 - \text{RH}) K_w}{K_n \beta_n \lambda_z [\text{NH}_3]} \quad (2.22)$$

In order to obtain the large applicability of the model regardless of the magnitude of the ammonia gradient. The model developed by Freiberg (1978) was based on the assumptions that  $[\text{NH}_3]$  was constant in each elliptical plume ring during plume expansion. To the extent that the ammonia gradient was small (i.e. insofar as  $\text{NH}_3$  has penetrated the plume), the applicability of the model was good, whether or not the oxidation process required ammonia as a buffer.

Panich (1980) studied the neutralization of primary sulfuric acid in power plant plumes by traces concentration of ambient ammonia. It was concluded that due to the absorption of ammonia by the acid particles, ammonia concentration profile resembled an inverse Gaussian profile with the lowest point at the plume center line (where the acid concentration was at the highest). The initial ambient ammonia concentration affected the rate of neutralization by providing more of the ammonia molecules per unit volume of entrained air to the surface of the acid particle; thus, the high initial ambient ammonia concentration speeded up the rate of neutralization directly.

Behra et al. (1989) studied dominating influence of ammonia on the oxidation of aqueous sulfur dioxide: the coupling of ammonia and sulfur dioxide in atmospheric water. They stated that the oxidation of sulfur dioxide in atmospheric water (cloud, rain, liquid aerosol and fog) was influenced by the presence of ammonia. The enhancing effect of ammonia was especially pronounced if the oxidation occurred with an oxidant such as ozone for which the reaction rate increased strongly with increasing pH, because ammonia codetermined the pH of the water and thus in turn the solubility of sulfur dioxide and provided acid neutralizing capacity as well as buffer intensity to the heterogeneous atmosphere-water system in counteracting the acidity produced by the oxidation of sulfur dioxide. At low buffer intensity, the acidity production led to the alleviation of further sulfur dioxide oxidation.