Chapter III

Methodology

The development of the mathematical model of sulfur dioxide oxidation in plume using the Monte Carlo method for a single point source and flat terrain consists of 5 steps as described below :

3.1 Development of mathematical model of sulfur dioxide oxidation in plume using the Monte Carlo method

3.2 Verification of mass conservation of mathematical model of sulfur dioxide oxidation in plume using the Monte Carlo method

3.3 Evaluation of the values of the simulated horizontal and vertical dispersion coefficients in comparison to Pasquill-Gifford dispersion coefficients

3.4 Application of mathematical model of sulfur dioxide oxidation in plume using the Monte Carlo method to a stack of the South Bangkok Power Plant in Samut Prakarn

3.5 Sensitivity analysis of chemical reactions of mathematical model of sulfur dioxide oxidation in plume using the Monte Carlo method with a stack of the South Bangkok Power Plant in Samut Prakarn

3.1 Development of Mathematical Model of Sulfur Dioxide Oxidation in Plume Using the Monte Carlo Method

The characteristics of the mathematical model of sulfur dioxide oxidation in plume using the Monte Carlo method are based on "Physico-Chemical" mathematical model which comprises 2 major components, which are:

3.1.1 Physical mathematical model

3.1.2 Chemical reaction mathematical model

3.1.1 Description of Physical Mathematical Model

The 3-dimensional physical mathematical model is used to calculate sulfur dioxide and sulfate aerosol movements. The motion in the x direction is the result from advection by wind. The movements in y and z directions are the consequence of dispersions. Using the Monte Carlo approach to simulate advection and dispersion, we divided the atmospheric volume into cells which sulfur dioxide and sulfate aerosol quanta move into, where the dimension of each cell is equivalent to 100x100x100 m . The location of pollutant emission source and meteorological data are put into the mathematical model for particle path calculations. The details of the physical mathematical model are as follows:

3.1.1.1 Advection

Advection is the movement resulting from wind velocity. Therefore, the location of pollutant emission source, time step and wind velocity are the primary data for advective calculation.

The steps of advective simulation are composed of :

a) defining the initial locations of sulfur dioxide and sulfate aerosol quanta; (m) and then dividing them by the width of the cell for unit conversion from meter to cell.

b) defining the wind velocity; (m/s) and then dividing it by the width of the cell for unit conversion from meter/s to cell/s.

c) defining the time step; (s/time).

d) calculating the new location which equals the initial location + (wind velocity * time step).

e) the new locations of sulfur dioxide and sulfate aerosol quanta assigned to the nearest cell during each time step by generating a random number from 0 to 1 in order to make a decision that the new locations of sulfur dioxide and sulfate aerosol quanta should be at which cell.

For example, if the initial location of sulfur dioxide quantum, wind velocity and time step equal 0 cell, 1.2 cell/s and 1 s/time, respectively. Thus, the new location of sulfur dioxide quantum is at 1.2 cell; meaning that sulfur dioxide quantum has 80% probability to stay at the first cell and 20% probability to stay at the second cell. Therefore, a random number is generated to make a decision that sulfur dioxide quantum should be at the first or the second cell. The random number generated is assumed to be 0.85; meaning that the new location of sulfur dioxide quantum is at the second cell.

3.1.1.2 Dispersion

Dispersions are the motions caused from the simulated horizontal and vertical dispersion coefficients. So the location of pollutant emission source, the atmospheric stability class, the downwind distance, and the simulated horizontal and vertical dispersion coefficients are the basic data for dispersing simulation.

Dispersions in the horizontal and vertical directions are assumed to be Gaussian dispersions. Consequently, the concentrations of pollutants emitted disperse like normal distribution of which sysmetrical bell-shaped area under the curve is equivalent to 1.

From Figure 3.1, the maximum concentrations of pollutants are located at the plume center and the overall area under the curve equals 1.

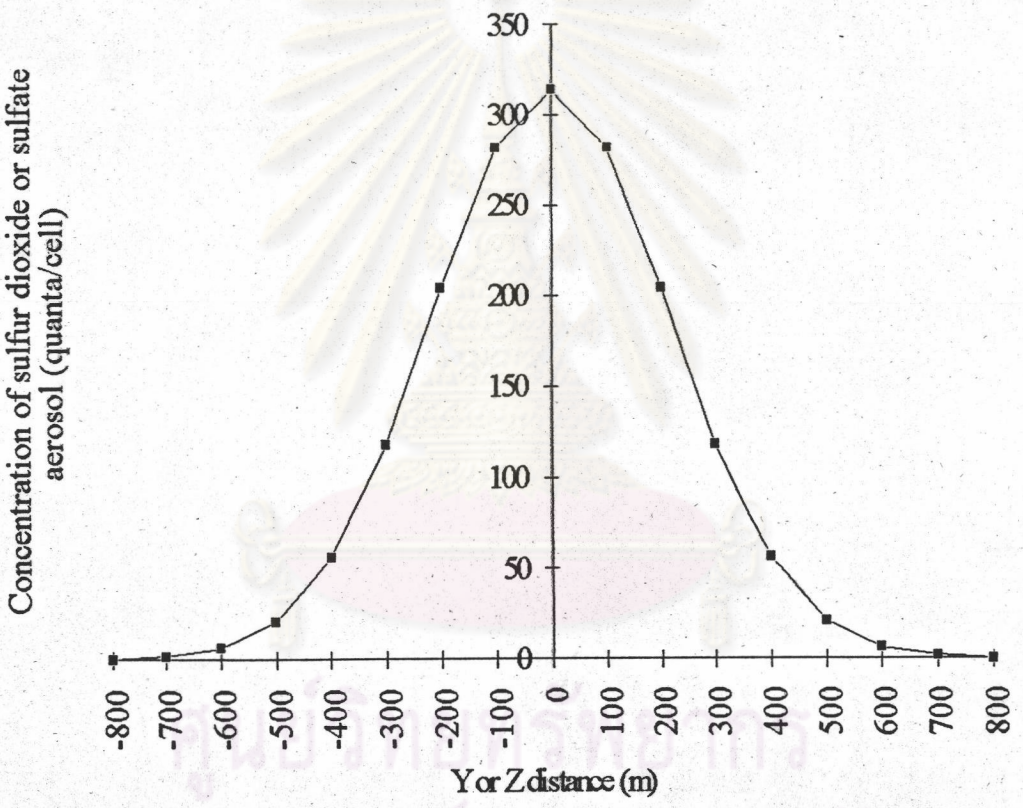


Figure 3.1 Dispersion of Sulfur Dioxide or Sulfate Aerosol Concentration in Y or Z Direction

The concept of using the Monte Carlo approach to the simulations of horizontal and vertical dispersions is described as follows: Every quantum of pollutant initially clusters with each other at the plume center. After that, each quantum has 50% probability to move to the left or to the right of the plume center (horizontal

movement) and 50% probability to move to the top or to the bottom of the plume center (vertical movement). So the random method is used to simulate the dispersions. The random dispersion is identical to Brownian diffusion but the dispersion of atmospheric pollutant results from Eddy current that makes pollutant scattering in a different manner, which is much faster than the molecular Brownian motion.

The stages of dispersing simulation are made up of :

a) defining the initial locations of sulfur dioxide and sulfate aerosol quanta; (m) and then dividing them by the length and height of cells for unit conversions from meters to cells.

b) defining the atmospheric stability class and downwind distance in order to find the simulated horizontal and vertical dispersion coefficients; (m) and then dividing them by the length and height of cells for unit conversions from meters to cells.

c) first generating a random number from 0 to 1 which is used to determine where sulfur dioxide and sulfate aerosol quanta move to the left or the right from the initial cell (horizontal movement) and move to the top or to the bottom from the initial cell (vertical movement). If the random number is more than 0.5, sulfur dioxide and sulfate aerosol quanta go to the right (horizontal movement) and go to the top (vertical movement). On the other hand, If the random number is less than 0.5, sulfur dioxide and sulfate aerosol quanta go to the left (horizontal movement) and go to the bottom (vertical movement). In fact, every quantum must move from the plume center to the either side. If the random number is equivalent to 0.5, the procedure of generating random number is repeated until it does not equal 0.5.

d) calculating the new locations of sulfur dioxide and sulfate aerosol quanta:

• If a random number is more than 0.5

the new location = the initial location + the simulated horizontal dispersion coefficient (horizontal movement)

or

the new location = the initial location + the simulated vertical dispersion coefficient (vertical movement)

• If a random number is less than 0.5

the new location = the initial location - the simulated horizontal dispersion coefficient (horizontal movement)

or

the new location = the initial location - the simulated vertical dispersion coefficient (vertical movement)

e) the new locations of sulfur dioxide and sulfate aerosol quanta assigned to the nearest cell during each time step by generating a random number from 0 to 1 in order to decide that the new locations of sulfur dioxide and sulfate aerosol quanta should be at which cell.

For example, if the initial location of sulfur dioxide quantum, the atmospheric stability class, the downwind distance and the simulated horizontal dispersion coefficient in case of the horizontal movement equal 1 cell, class E, 10 km and 0.3 cell, respectively, subsequently, a random number is first generated (assumed to be 0.7). So sulfur dioxide quantum goes to the right and the new location is at 1.3 cell. Thus, sulfur dioxide quantum has 70% probability to stay at the first cell and 30% probability to stay at the second cell. The random number is then generated to decide whether sulfur dioxide quantum should be at the first or the second cell. The random number second generated is assumed to be 0.75; meaning that the new location of sulfur dioxide quantum is at the second cell.

3.1.2 Description of Chemical Reaction Mathematical Model

After each sulfur dioxide quantum is advected and dispersed to its new location at each time step, the chemical reaction mathematical model is used to determine the rate of sulfur dioxide oxidation in plume using the Monte Carlo method.

The rates of sulfur dioxide oxidations are divided into 2 types:

3.1.2.1 The first order reaction rate of sulfur dioxide oxidation

3.1.2.2 The non-first order reaction rate of sulfur dioxide oxidation

3.1.2.1 The First Order Reaction Rate of Sulfur Dioxide Oxidation

The first order reaction rate of sulfur dioxide oxidation is:

$$\frac{d[SO_4^{2-}]}{dt} = K[SO_2] \qquad (3.1)$$

where

$\frac{d[SO_4^{2-}]}{dt}$ = sulfate formation rate; (mole/m^3-s)

K = reaction rate constant; $(s)^{-1}$

$[SO_2]$ = sulfur dioxide concentration; (mole/m^3)

From Equation (3.1), the calculation of sulfate formation rate of each sulfur dioxide quantum which is at the new location relies on the reaction rate constant. The reaction rate constant and time step are the elementary data for the calculation of sulfate formation rate.

The procedures of the calculation of sulfate formation rate consist of :

a) defining the time step; (s/time).

b) defining the reaction rate constant; $(s)^{-1}$.

c) calculating the reaction rate constant during time step which equals time step * reaction rate constant.

d) generating a random number from 0 to 1 which is used to determine the sulfate formation rate.

For example, the time step and the reaction rate constant are equivalent to 20 s and 0.01 per hour, respectively. So the reaction rate constant during time step is 5.56×10^{-5}(0.01*20/3600). A random number is subsequently generated. If the random number is more than 5.56×10^{-5}, sulfur dioxide quantum doesn't convert to sulfate aerosol quantum. If the random number is less than 5.56×10^{-5}, sulfur dioxide quantum transforms to sulfate aerosol quantum. The random number generated is assumed to be 2.5×10^{-5}; meaning that sulfur dioxide quantum converts to sulfate aerosol quantum.

The concept described above is applied to Brimblecombe and Spedding (1974)'s reaction rate which is written in the form:

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

The probability of sulfur dioxide to sulfate transformation for Brimblecombe and Spedding (1974)'s reaction rate is:

$$\frac{-d[S(IV)]}{dt[S(IV)]} = K[Fe(III)] \quad ;(s)^{-1} \qquad (3.2)$$

So the reaction rate constant during a time step is equivalent to time step * reaction rate constant * Iron(III) concentration. This value is used to predict the sulfate formation.

3.1.2.2 The Non-First Order Reaction Rate of Sulfur Dioxide Oxidation

Panich (1983) proposed an idea of the calculation of sulfate formation for non-first order reaction of sulfur dioxide oxidation as described below.

The non-first order reaction rate of sulfur dioxide oxidation is:

$$\frac{d[SO_4^{2-}]}{dt} = K[SO_2]^n[P]^m \qquad (3.3)$$

where

$\frac{d[SO_4^{2-}]}{dt}$ = sulfate formation rate; (mole/m^3-s)

K = reaction rate constant; $(s)^{-1}(mole/m^3)^{1-n-m}$

$[SO_2]$ = sulfur dioxide concentration; (mole/m^3)

[P] = oxidizing agent or inert substance or catalyst concentration; (mole/m^3)

n = n^{th} order with respect to sulfur dioxide concentration ($n \neq 1$)

m = m^{th} order with respect to oxidizing agent or inert substance or catalyst concentration

From Equation (3.3), the calculation of sulfate formation rate of each sulfur dioxide quantum which is at the new location depends on the reaction rate constant, the sulfur dioxide concentration, the oxidizing agent or inert substance or catalyst concentration, the n^{th} order with respect to sulfur dioxide concentration and the m^{th} order with respect to the oxidizing agent or inert substance or catalyst concentration. So the probability of sulfur dioxide to sulfate transformation is used to calculate sulfate formation for the non-first order reaction rate. The formula of the probability of sulfur dioxide to sulfate transformation is :

$$P = \frac{-d[SO_2]}{dt[SO_2]} = \frac{d[SO_4^{2-}]}{dt[SO_2]} = \frac{K[SO_2]^n}{[SO_2]} = K[SO_2]^{n-1} \quad (3.4)$$

where

P = probability of sulfur dioxide to sulfate transformation of each sulfur dioxide quantum

For example, there are 5 sulfur dioxide quanta released into the atmosphere. Suppose that the first sulfur dioxide quantum moves into the first cell. The rest of sulfur dioxide quanta possibly move into the first cell. As each sulfur dioxide quantum undergoes the transport calculation step and the subsequent kinetic reaction rate calculation step at the same time step, it is impossible to know whether the other quanta will move into the same cell point or not. The probability of the first sulfur dioxide quantum oxidized to sulfate can be calculated from the first order reaction rate. The probability is :

$$P1 = K[SO_2]^{n-1} = K[1]^{n-1} = K \qquad (3.5)$$

P1 = probability of sulfur dioxide to sulfate transformation of the first sulfur dioxide quantum

If the second sulfur dioxide quantum moves into the first cell like the first sulfur dioxide quantum. The probability of the both sulfur dioxide quanta oxidized to sulfate is :

$$Ptotal = K[SO_2]^{n-1} = K[2]^{n-1} \qquad (3.6)$$

Ptotal = probability of sulfur dioxide to sulfate transformation of the both sulfur dioxide quanta

Therefore, the probability of sulfur dioxide to sulfate transformation of the second sulfur dioxide quantum is :

$$\begin{aligned} P2 &= 2Ptotal - P1 \\ &= 2K[2]^{n-1} - K \\ &= K[2^n - 1] \end{aligned} \qquad (3.7)$$

P2 = probability of sulfur dioxide to sulfate transformation of the second sulfur dioxide quantum

. If the other sulfur dioxide quanta move into the first cell, the probability of sulfur dioxide to sulfate transformation of the total sulfur dioxide quanta in the first cell and of the sulfur dioxide quantum entering into the first cell are determined. These values are represented into Table 3.1.

Table 3.1 The Probability of Sulfur Dioxide to Sulfate Transformation for the Non-First Order Reaction Rate

Number of sulfur dioxide quanta entering into the cell point at any time	The probability of sulfur dioxide to sulfate transformation of each sulfur dioxide quantum entering into the cell point	The probability of sulfur dioxide to sulfate transformation of total sulfur dioxide quanta entering into the cell point
1	K	K
2	$K(2^n-1)$	$K(2)^{n-1}$
3	$K(3^n-2^n)$	$K(3)^{n-1}$
.	.	.
.	.	.
.	.	.
num	$K[(num)^n-(num-1)^n]$	$K(num)^{n-1}$

The processes of the calculation of sulfate formation rate consist of :

a) defining the time step; (s/time).

b) defining the reaction rate constant; $(s)^{-1}(mole/m^3)^{1-n}$.

c) defining the probability of sulfur dioxide to sulfate transformation of each sulfur dioxide quantum entering into the cell point from Table 3.1.

d) calculating the reaction rate constant during time step which is equal to time step * the probability of sulfur dioxide to sulfate transformation of each sulfur dioxide quantum entering into the cell point.

e) generating a random number from 0 to 1 which is used to determine the sulfate formation rate.

. The concept described above is used to apply to Freiberg (1974)'s and Ibusuki, Ohsawa and Takeuchi (1990)'s reaction rates as below.

- **In Case of Freiberg (1974)'s Reaction Rate in Ammonia-Rich Environment**

Freiberg (1974)'s reaction rate is:

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

Let $C_1 = K_o\beta_s^2 K_s^2 \frac{[\beta_n K_n \lambda_z]^3}{[2(1-RH)K_w]^3}[Fe^{3+}][NH_3]^3$; (m^3/mole-min)

Substitute C_1 into Equation (2.16), we get

$$\frac{-d[SO_2]}{dt} = C_1[SO_2]^2 \qquad (3.8)$$

The probability of sulfur dioxide to sulfate transformation for Freiberg (1974)'s reaction rate is:

$$\frac{-d[SO_2]}{dt[SO_2]} = C_1[SO_2] \qquad (3.9)$$

Let sulfur dioxide emission rate, the number of sulfur dioxide quanta and time step be Q g/s, N quanta and t s/time, respectively. So one quantum equals $\frac{Q*t}{N}$ g of sulfur dioxide. Since the unit of sulfur dioxide concentration in the physico-chemical mathematical model is quantum/cell, the C_1 value is multiplied by $\frac{Q*t*10^{-6}}{N*3840}$ for unit conversion from (m^3/mole-min) to (cell/quantum-s).

For unit conversion, Equation (3.9) is changed to:

$$\frac{-d[SO_2]}{dt[SO_2]} = C_1 * \frac{Q*t*10^{-6}}{N*3840} * [SO_2] \qquad (3.10)$$

When the probability of sulfur dioxide to sulfate transformation for Freiberg (1974)'s reaction rate is defined, we can proceed with the processes of the calculation of sulfate formation rate as explained above.

- **In Case of Ibusuki, Ohsawa and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment**

Ibusuki et al. (1990)'s reaction rate is:

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

Freiberg (1974) defined the relationship between hydrogen ion concentration and ammonia concentration as shown below:

$$[H^+] = \frac{2(1-RH)K_w}{K_n\beta_n\lambda_z[NH_3]} \qquad (2.22)$$

The substitution of Equation (2.22) into Equation (2.17) yields:

$$\frac{-d[S(IV)]}{dt} = K[S(IV)]^2[Fe^{2+}]^{0.5}\left[\frac{2(1-RH)K_w}{K_n\beta_n\lambda_z[NH_3]}\right]^{-0.5} \qquad (3.11)$$

The probability of sulfur dioxide to sulfate transformation for Ibusuki et al. (1990)'s reaction rate is:

$$\frac{-d[S(IV)]}{dt[S(IV)]} = K[S(IV)][Fe^{2+}]^{0.5}\left[\frac{2(1-RH)K_w}{K_n\beta_n\lambda_z[NH_3]}\right]^{-0.5} \qquad (3.12)$$

Let $C_2 = K[Fe^{2+}]^{0.5}\left[\frac{2(1-RH)K_w}{K_n\beta_n\lambda_z[NH_3]}\right]^{-0.5}$; $(m^3/mole\text{-}s)$

The substitution of C_2 into Equation (3.12) yields:

$$\frac{-d[S(IV)]}{dt[S(IV)]} = C_2[S(IV)] \qquad (3.13)$$

The C_2 value is multiplied by $\frac{Q*t*10^{-6}}{N*64}$ for unit conversion from (m^3/mole-s) to (cell/quantum-s).

For unit conversion, Equation (3.13) is changed to:

$$\frac{-d[S(IV)]}{dt[S(IV)]} = C_2*\frac{Q*t*10^{-6}}{N*64}*[S(IV)] \qquad (3.14)$$

When the probability of sulfur dioxide to sulfate transformation for Ibusuki et al. (1990)'s reaction rate is defined, we can proceed with the processes of the calculation of sulfate formation rate as explained above.

For both reaction rates, the ammonia concentrations included in C_1 and C_2 are defined as constants; as a result the ammonia concentrations are in excess with regard to sulfur dioxide concentration and enough to neutralize sulfate aerosol produced from the sulfur dioxide oxidation. Accordingly there is no ammonia gradient in this condition, hence termed as ammonia-rich environment. Ammonia-rich environment is defined by $[NH_3] > 2[H_2SO_4]$ where [ ] denotes molar concentration of the component (Saxena et al., 1986).

Flow chart illustrates the physico-chemical mathematical model for Brimblecombe and Spedding (1974)'s reaction rate, Freiberg (1974)'s reaction rate in ammonia-rich environment and Ibusuki et al., (1990)'s reaction rate in ammonia-rich environment as depicted in Figure 3.2.

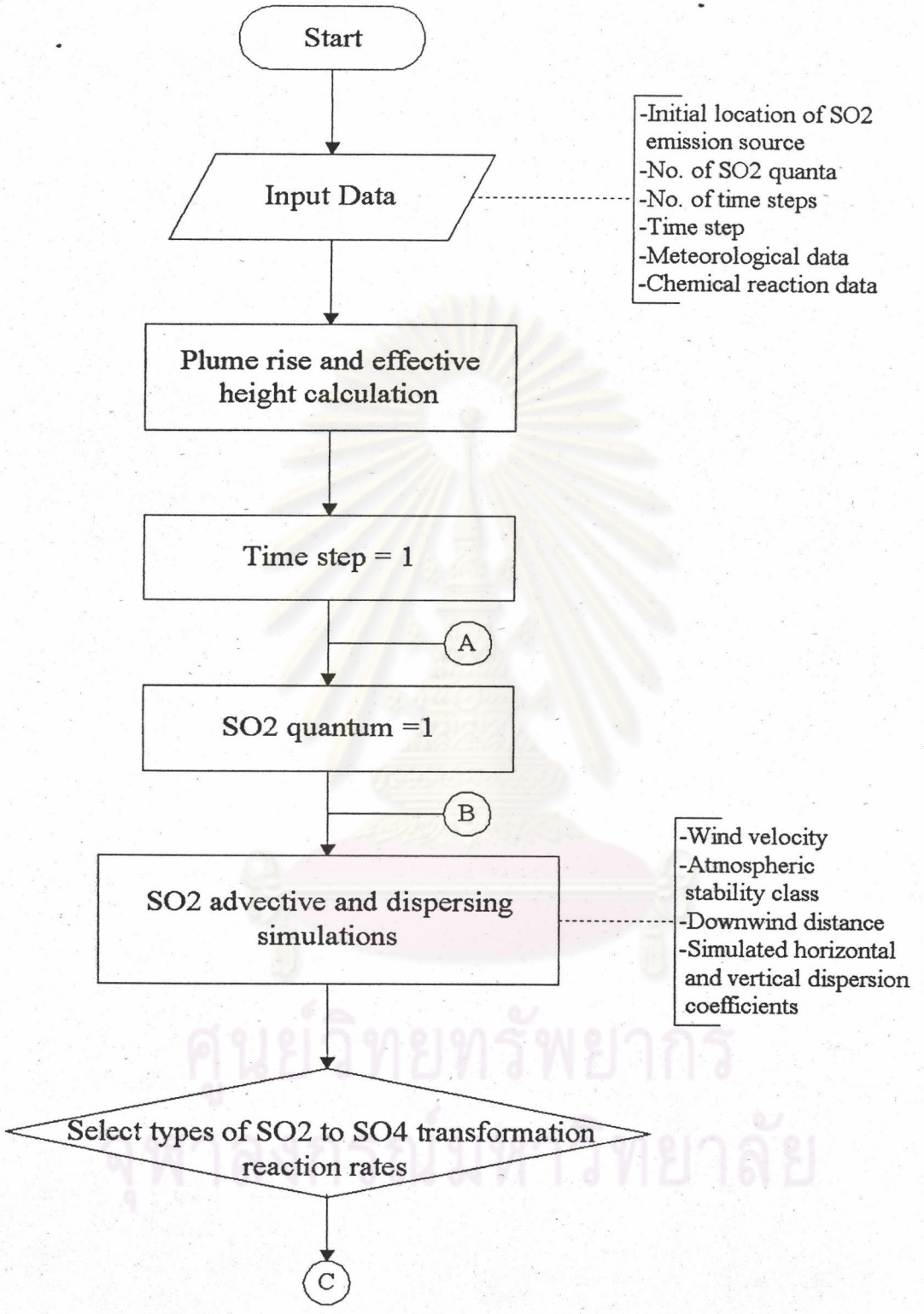


Figure 3.2 Flow Chart of the Physico-Chemical Mathematical Model for Brimblecombe and Spedding (1974)'s Reaction Rate, Freiberg (1974)'s Reaction Rate in Ammonia-Rich Environment and Ibusuki et al., (1990)'s Reaction Rate in Ammonia-Rich Environment

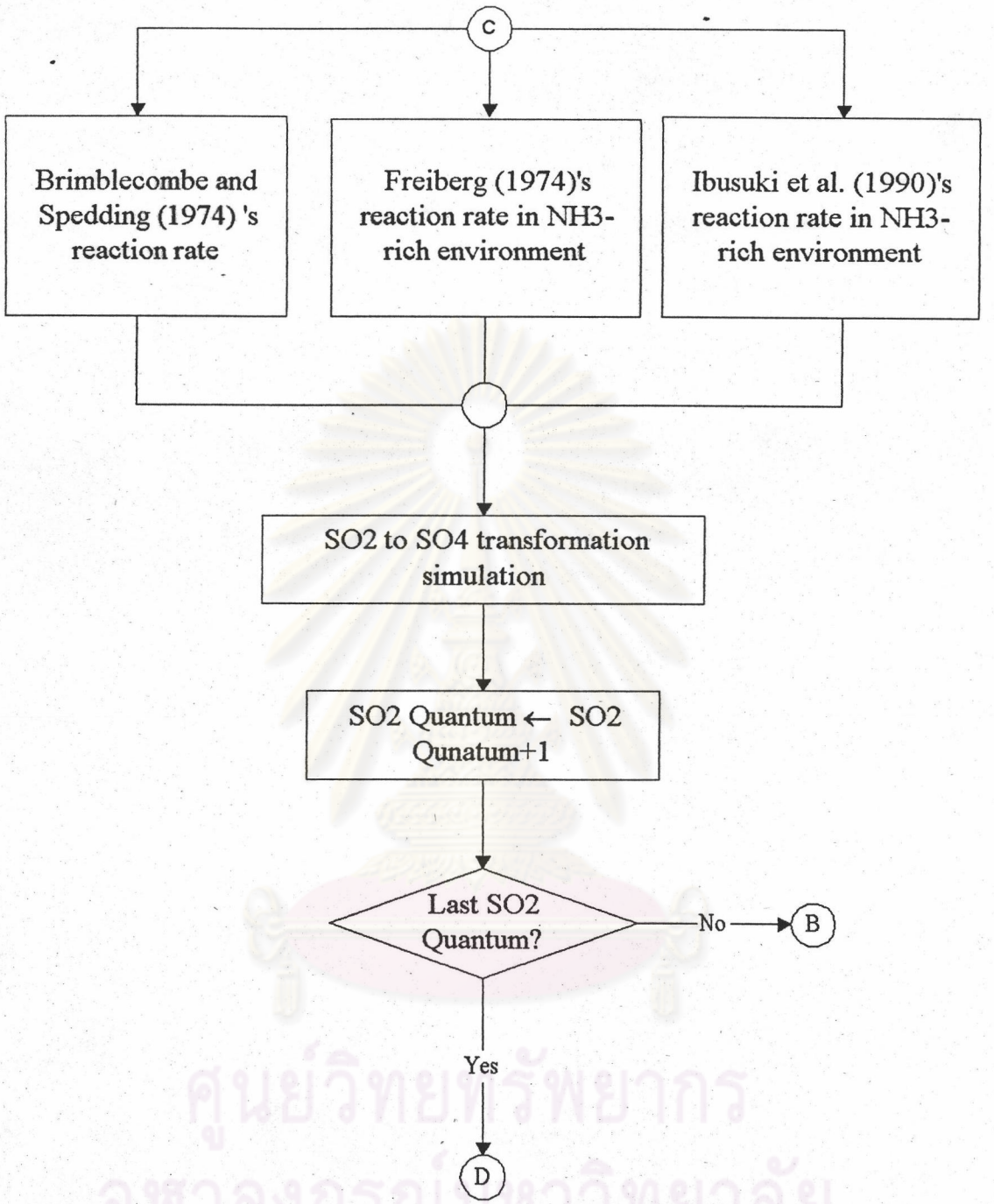
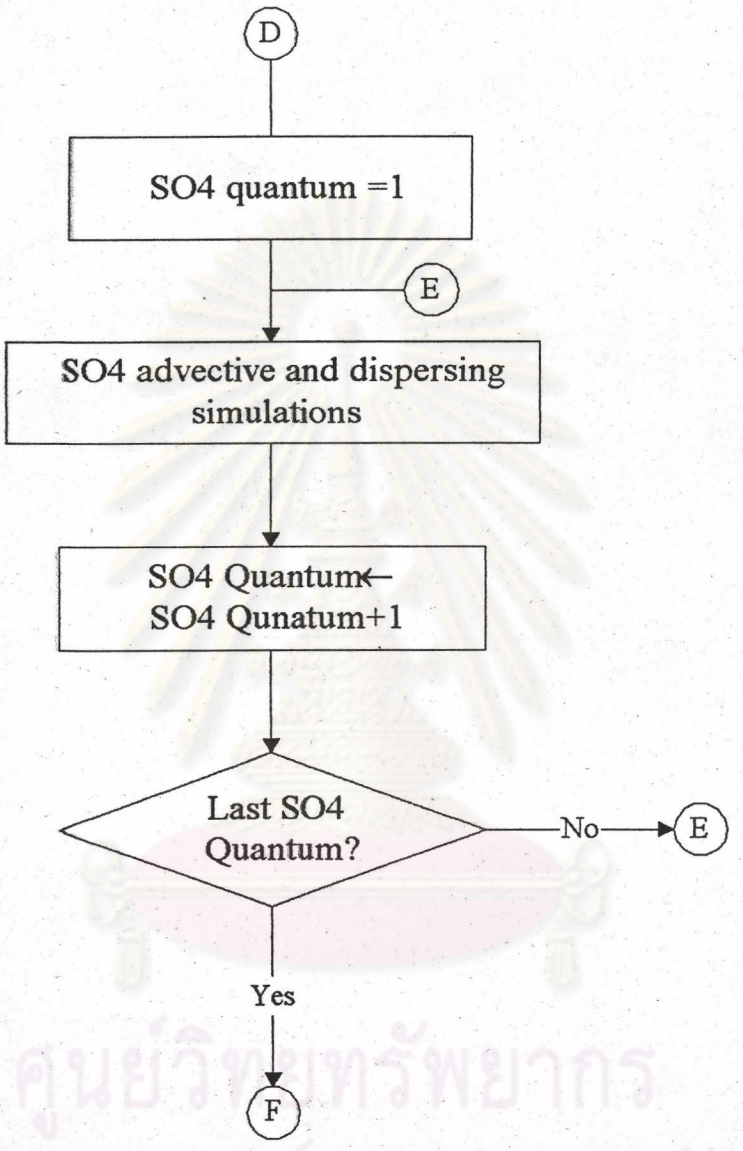


Figure 3.2 Flow Chart of the Physico-Chemical Mathematical Model for Brimblecombe and Spedding (1974)'s Reaction Rate, Freiberg (1974)'s Reaction Rate in Ammonia-Rich Environment and Ibusuki et al., (1990)'s Reaction Rate in Ammonia-Rich Environment (Continued)



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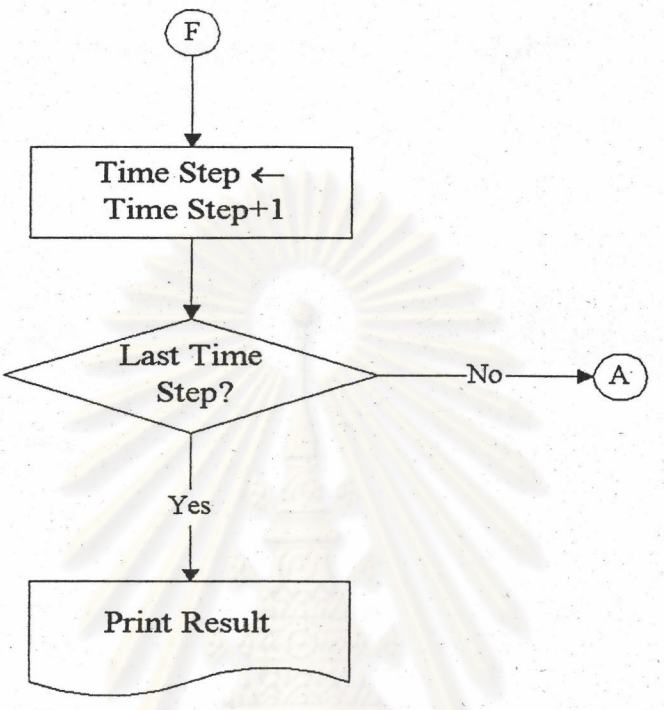

Figure 3.2 Flow Chart of the Physico-Chemical Mathematical Model for Brimblecombe and Spedding (1974)'s Reaction Rate, Freiberg (1974)'s Reaction Rate in Ammonia-Rich Environment and Ibusuki et al., (1990)'s Reaction Rate in Ammonia-Rich Environment (Continued)

- **In Case of Freiberg (1974)'s Reaction Rate in Ammonia-Deficient Environment**

Ammonia-deficient environment is defined by $[NH_3] \leq 2[H_2SO_4]$ where [ ] denotes molar concentration of the component (Saxena et al., 1986). So ammonia limitation is considered whereas the sulfur dioxide oxidation is occuring. Behra et al., (1989) stated that we can expect in atmospheric water droplets (cloud, rain, liquid aerosols) relatively constant proportion of NH_4^+ to SO_4^{2-} (mol-ratio $[NH_4^+]/[SO_4^{2-}] \approx 2$). Consequently, ammonia and sulfuric acid in equilibrium with a wet aerosol (RH>80%) is expressed as follows:

$$2NH_3(g) + H_2SO_4(aq) \leftrightarrow (NH_4)_2SO_4(aq) \qquad (3.15)$$

From Equation (3.15), 2 moles of ammonia react completely with 1 mole of sulfate. Thus, mass conservation of ammonia at any given time holds on the following relationship:

$$[NH_3]_{remaining} = [NH_3]_o - [NH_3]_{react} \qquad (3.16)$$

or

$$[NH_3]_{remaining} = [NH_3]_o - 2[SO_4^{2-}] \qquad (3.17)$$

where

$[NH_3]_{remaining}$ = remaining concentration of ammonia; (mole/m^3)

$[NH_3]_o$ = initial concentration of ammonia; (mole/m^3)

$[NH_3]_{react}$ = reacting concentration of ammonia; (mole/m^3)

$[SO_4^{2-}]$ = concentration of sulfate; (mole/m^3)

The physico-chemical mathematical model based on the concept as illustrated above for Freiberg (1974)'s reaction rate in ammonia-deficient environment is modified as follows: First, each sulfate aerosol quantum is advected and dispersed to its new location where each cell has $[SO_4^{2-}] \leq \frac{1}{2}[NH_3]$. If each cell has $[SO_4^{2-}] > \frac{1}{2}[NH_3]$,

the procedures of advective and dispersing simulations are repeated until each cell has $[SO_4^{2-}] \leq \frac{1}{2}[NH_3]$. Then, each sulfur dioxide quantum is advected and dispersed to its new location where each cell is checked whether the remaining concentrations of ammonia are more than or equal to twice as many as concentrations of sulfate or not. If each cell has $[NH_3]_{remaining} \geq 2[SO_4^{2-}]$, the probability of sulfur dioxide to sulfate transformation of each sulfur dioxide quantum entering into the cell point is determined to predict the sulfate formation. Ammonia concentration included in the C_1 value (see Equation (3.9)) varies with sulfate concentration (see Equation (3.17)). So the C_1 value in ammonia-deficient environment is always less than the C_1 value in ammonia-rich environment. On the contrary, if each cell has $[NH_3]_{remaining} < 2[SO_4^{2-}]$, the sulfur dioxide oxidation in aqueous phase does not occur.

Figure 3.3 shows the flow chart illustrating the physico-chemical mathematical model for Freiberg (1974)'s reaction rate in ammonia-deficient environment.

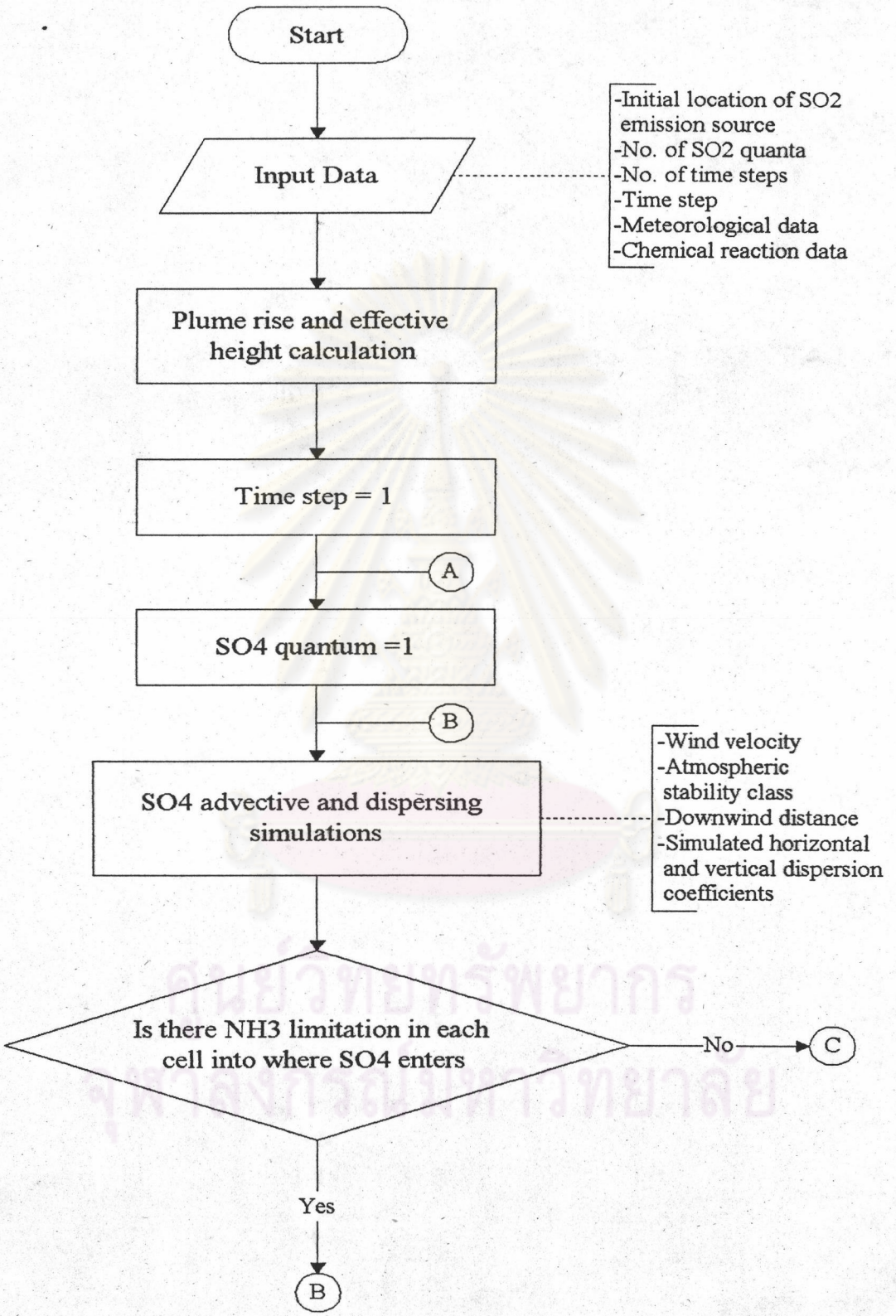

Figure 3.3 Flow Chart of the Physico-Chemical Mathematical Model for Freiberg (1974)'s Reaction Rate in Ammonia-Deficient Environment

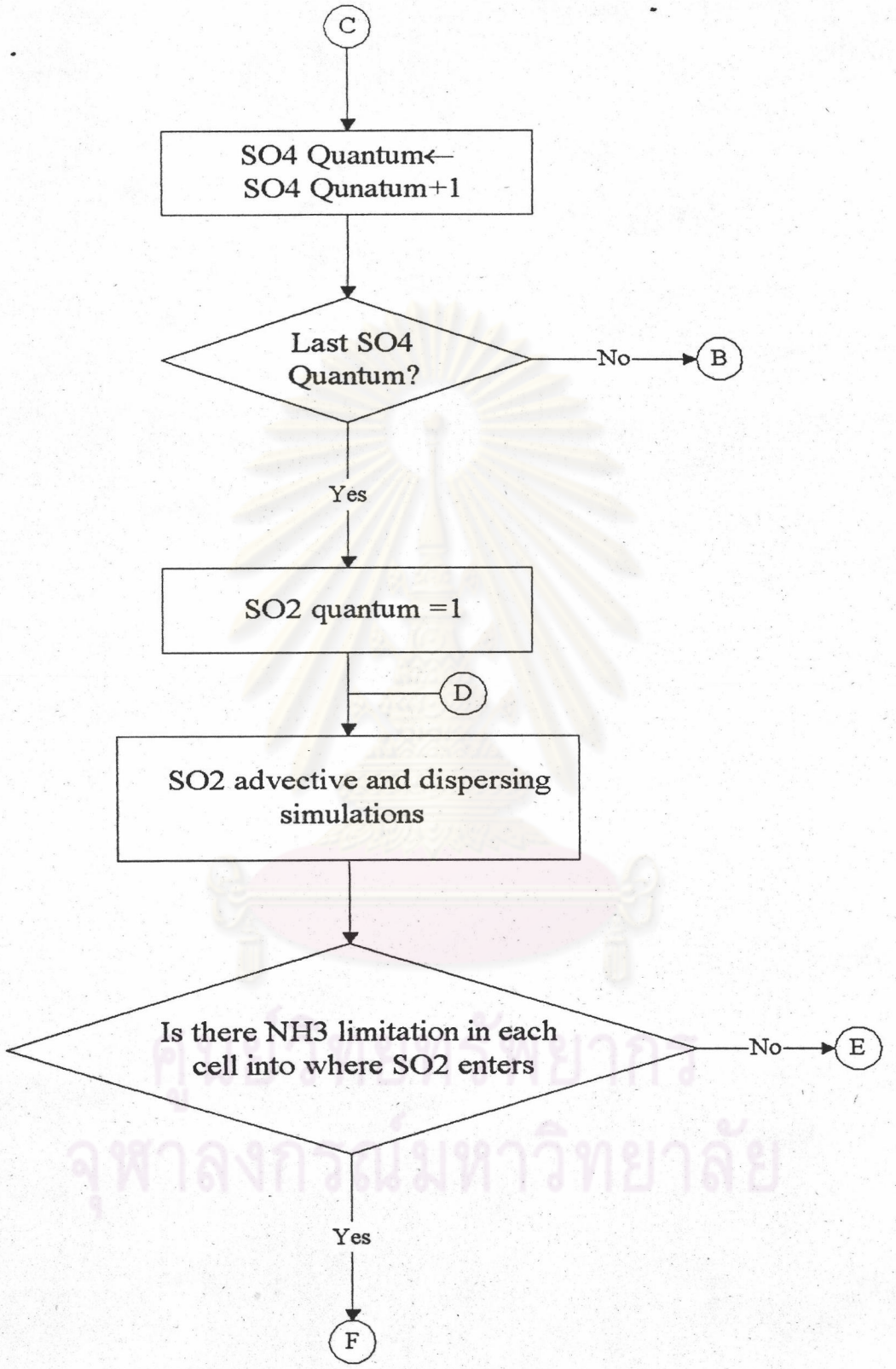

Figure 3.3 Flow Chart of the Physico-Chemical Mathematical Model for Freiberg (1974)'s Reaction Rate in Ammonia-Deficient Environment (Continued)

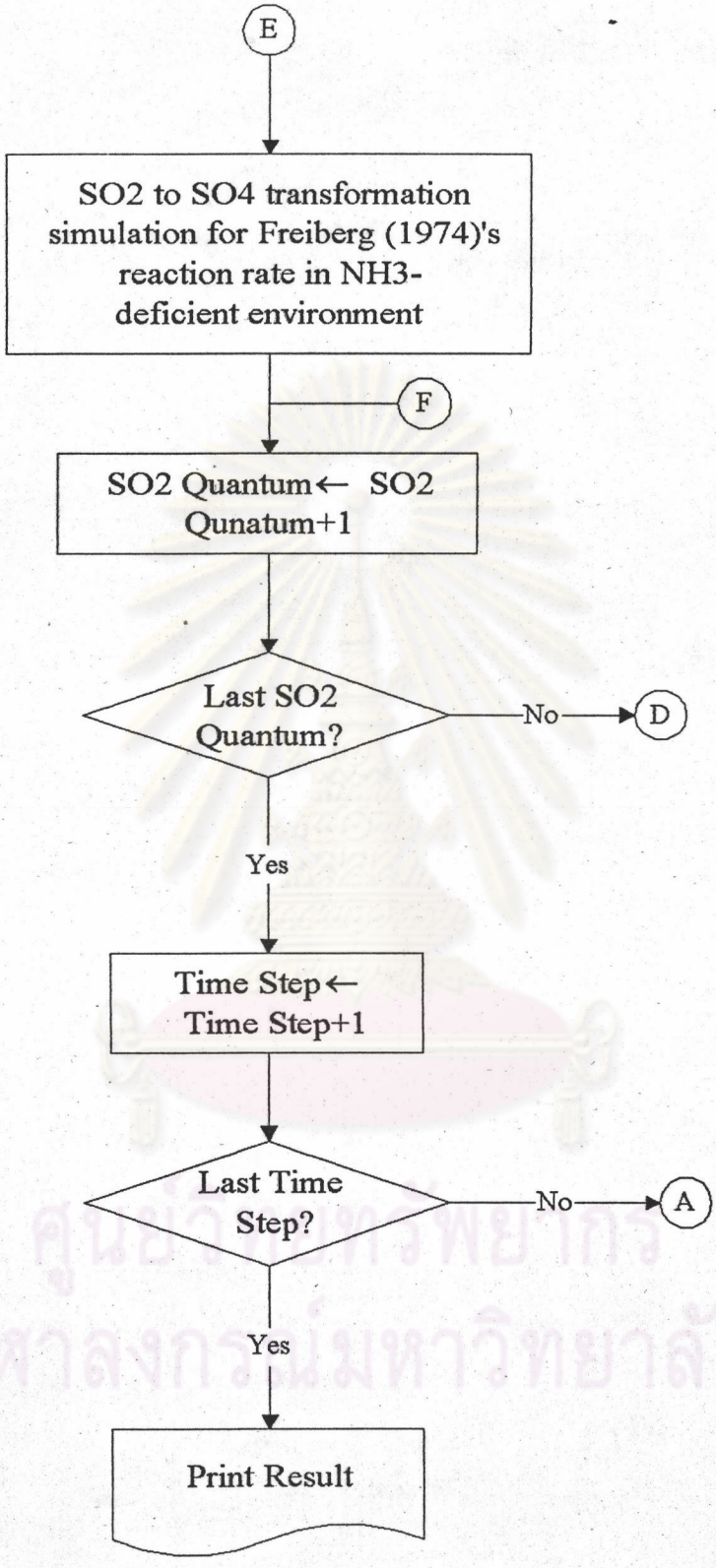

Figure 3.3 Flow Chart of the Physico-Chemical Mathematical Model for Freiberg (1974)'s Reaction Rate in Ammonia-Deficient Environment (Continued)

3.2 Verification of Mass Conservation of Mathematical Model of Sulfur Dioxide Oxidation in Plume Using the Monte Carlo Method

We consider the atmospheric volume into where sulfur dioxide and sulfate aerosol quanta move at any given time. Mass balance of sulfur dioxide and sulfate aerosol quanta in the cells is:

$$SO_{2,in} + SO_4^{2-}{}_{,in} - SO_{2,out} - SO_4^{2-}{}_{,out} = SO_{2,acc} + SO_4^{2-}{}_{,acc} \quad (3.18)$$

$$(SO_2 + SO_4^{2-})_{in} = (SO_2 + SO_4^{2-})_{out} + (SO_2 + SO_4^{2-})_{acc} \quad (3.19)$$

where

$SO_{2,in}, SO_4^{2-}{}_{,in}$ = sulfur dioxide and sulfate aerosol quanta moving into cells, respectively.

$SO_{2,out}, SO_4^{2-}{}_{,out}$ = sulfur dioxide and sulfate aerosol quanta moving out of cells, respectively.

$SO_{2,acc}, SO_4^{2-}{}_{,acc}$ = sulfur dioxide and sulfate aerosol quanta accumulating into cells,respectively.

The verification of mass conservation of mathematical model of sulfur dioxide oxidation in plume using the Monte Carlo method is based on Equation (3.19). If mass conservation does not correspond with mass balance equation, the number of cells must be larger in order to account for all of sulfur dioxide and sulfate aerosol quanta.

3.3 Evaluation of the Values of the Simulated Horizontal and Vertical Dispersion Coefficients in Comparison to Pasquill-Gifford Dispersion Coefficients

The principle of evaluation of the simulated horizontal and vertical dispersion coefficients is that the under curve areas of the numerically calculated concentrations of sulfur dioxide are close to the under curve areas of the empirical concentrations of sulfur dioxide at the same criteria. There are 2 main procedures for evaluation of the simulated horizontal and vertical dispersion coefficients as illustrated below:

3.3.1 Calculation of the empirical concentrations of sulfur dioxide

3.3.2 Calculation of the numerical concentrations of sulfur dioxide

Both of the calculation of sulfur dioxide concentration profiles are computed for every atmospheric stability (Class A, B, C, D, E and F) at 1, 5 and 10 km downwind from the source.

3.3.1 Calculation of the Empirical Concentrations of Sulfur Dioxide

The details are as follows:

a) let sulfur dioxide emission rate be 500 g/s.

b) let average wind velocities at stack height be 2, 4, 5, 5, 2 and 2 m/s for atmospheric stability class A, B, C, D, E and F, respectively (see Table 2.1).

c) find the horizontal and vertical dispersion coefficients at 1, 5 and 10 km downwind from the source for every atmospheric stability class from Pasquill-Gifford curve (see Figure 2.2).

d) calculate the sulfur dioxide concentrations from Gaussian plume equation for a point source and no plume reflection from ground level. The equation (Slade, 1968) is defined as

$$C(x,y,z) = \frac{Q}{2\pi \bar{u}\sigma_y \sigma_z} \exp\left[\frac{-1}{2}\left\{\frac{y^2}{\sigma_y^2} + \frac{z^2}{\sigma_z^2}\right\}\right] \qquad (3.20)$$

where

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

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)

σ_y, σ_z = horizontal and vertical dispersion coefficients, respectively; (m)

e) the sulfur dioxide concentrations are computed by Equation (3.20) at any given y distance (z=0) and at any given z distance (y=0). Afterwards the empirical concentrations are multiplied by 10^6 for unit conversion from g/m^3 to g/cell. (1 cell = 10^6 m^3)

3.3.2 Calculation of the Numerical Concentrations of Sulfur Dioxide

Using physical mathematical model (item 3.1.1) to simulate the numerical concentrations of sulfur dioxide, the details are composed of:

a) defining the initial locations of sulfur dioxide; (m) and then dividing them by the width, length and height of cells for unit conversions from meters to cells.

b) defining the number of sulfur dioxide quanta emitted from the source; (quanta).

c) defining the time step; (s/time).

d) letting average wind velocities at stack height be 2, 4, 5, 5, 2 and 2 m/s for atmospheric stability class A, B, C, D, E and F, respectively (see Table 2.1).

e) assuming the horizontal and vertical dispersion coefficients (on trial and error basis) for every atmospheric stability class at 1, 5 and 10 km downwind from the source.

f) calculating the sulfur dioxide concentrations by using physical mathematical model. (Suppose that the number of sulfur dioxide quanta and the number of time step are equivalent to N quanta and t s/time, respectively. The sulfur dioxide emission rate in preceding section is equal to 500 g/s. So one quantum is equal to $\frac{500*t}{N}$ g of sulfur dioxide.) The numerical concentrations are then multiplied by $\frac{500*t}{N}$ for unit conversion from quanta/cell to g/cell.

g) comparing the under curve areas of the numerical concentrations of sulfur dioxide with the under curve areas of the empirical concentrations of sulfur dioxide at

any given y distance (z=0) and at any given z distance (y=0). If both concentration profiles have similar under curve areas, the assumed horizontal and vertical dispersion coefficients used are successful. On the contrary, if both concentration profiles have not similar under curve areas, the horizontal and vertical dispersion coefficients are reassumed until the under curve areas of the numerical concentration profiles fit closely to the under curve areas of the empirical concentration profiles.

3.4 Application of the Mathematical Model of Sulfur Dioxide Oxidation in Plume Using the Monte Carlo Method to a Stack of the South Bangkok Power Plant in Samut Prakarn

Before applying to a stack of the South Bangkok Power Plant, the mathematical model of sulfur dioxide oxidation in plume using the Monte Carlo method was additionally integrated in the vertical dispersion.

Plume touching the ground is considered in the vertical dispersion. We assume that the ground acts as a perfect reflector when plume touches the ground. So the perfect reflection condition of plume is added to the step d) in item 3.1.1.2 as detailed below:

• If a random number is less than 0.5

If the new location is the negative value, the perfect reflection of new location equals the absolute value of negative value.

After the calculation of the perfect reflection of new location, we proceed to simulate the vertical dispersion according to step e) in item 3.1.1.2 to determine the new location due to the perfect reflection.

3.5 Sensitivity Analysis of Chemical Reactions of the Mathematical Model of Sulfur Dioxide Oxidation in Plume Using the Monte Carlo Method with a Stack of the South Bangkok Power Plant in Samut Prakarn

There were 5 sulfur dioxide emission sources in the South Bangkok Power Plant but only the 5th source emitted sulfur dioxide resulting from fuel oil combustion in 1988. So the data of the 5th sulfur dioxide emission source are selected for simulation as summerized in Table 3.2.

Table 3.2 The Data of the 5th Sulfur Dioxide Emission Source (JICA, 1990)

Parameters	The 5th sulfur dioxide emission source
Operating Hours	24
Annual SO_2 (m^3/yr)**	918539
Flue Gas (m^3/hr)*	828564
Stack Height (m)	110
Stack Diameter(m)	5.0
Stack Exit Temperature (°C)	150

* at 25 °C and 101.325 KPa

** based upon 3% S content in fuel oil

The objectives of this section are to evaluate the simulated sulfate concentration in comparison to the measured sulfate concentration, and to study sensitivity analysis of chemical reactions of physico-chemical mathematical model influencing on sulfate formation by varing parameters such as atmospheric stability class, iron concentration, temperature, relative humidity and ammonia concentration.

The interested volume of studying plume released from the 5th source is about 10x8.5x3.5 km. The following chemical reactions are used to analyze sulfur dioxide oxidation in plume.

3.5.1 Brimblecombe and Spedding (1974)'s reaction rate is:

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

The parameters to be studied are

a) atmospheric stability class A, B, C, D, E and F which have wind velocities at stack height being 2, 4, 5, 5, 2 and 2 m/s, respectively (see Table 2.1).

b) measured iron concentration being 1201 ng/m^3 from JICA (1990) and high iron concentration being 0.1 mg/m^3 (100 μg/m^3).

3.5.2 Freiberg (1974)'s reaction rate is:

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

The parameters to be studied are

a) atmospheric stability class A, B, C, D, E and F which have wind velocities at stack height being 2, 4, 5, 5, 2 and 2 m/s, respectively (see Table 2.1).

b) measured iron concentration being 1201 ng/m^3 from JICA (1990) and high iron concentration being 0.1 mg/m^3 (100 μg/m^3).

c) temperature being 20, 25 and 30 °C.

d) relative humidity being 50, 70, 90, 95 and 99%

e) ammonia-rich environment

ammonia concentrations being 50, 80 and 100 ppb ([NH_3] = constant).

f) ammonia-deficient environment

initial ammonia concentrations being 50, 80 and 100 ppb.

Remark : Ammonia concentrations in both ammonia-rich environment and ammonia-deficient environment are assumed values as there were no measurements of ammonia in air available in Thailand. The values used here are thus based on very high side, but the range of 10-80 ppb has been used for the sulfur dioxide oxidation study. (Behra et al., 1989)

3.5.3 Ibusuki, Ohsawa and Takeuchi (1990)'s reaction rate is:

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

The parameters to be studied are the same as item 3.5.2 except item f).

For evaluation of simulated sulfate concentrations in comparison to measured sulfate concentrations, the measured sulfate concentrations in the dry season collected by Andersen Sampler method are compared with the simulated sulfate concentrations calculated from Freiberg (1974)'s reaction rate and Alkezweeny and Powell (1977)'s reaction rate. The measured sulfur dioxide and sulfate concentrations in Bang Na (MS1), located at 7 km away from the power plant (MS2) as shown in Figure 3.4, are summarized in Table 3.3. Freiberg's yields are simulated by mathematical model and Alkezweeny and Powell (1977)'s yield is calculated by using a rate of 0.1 per hour.

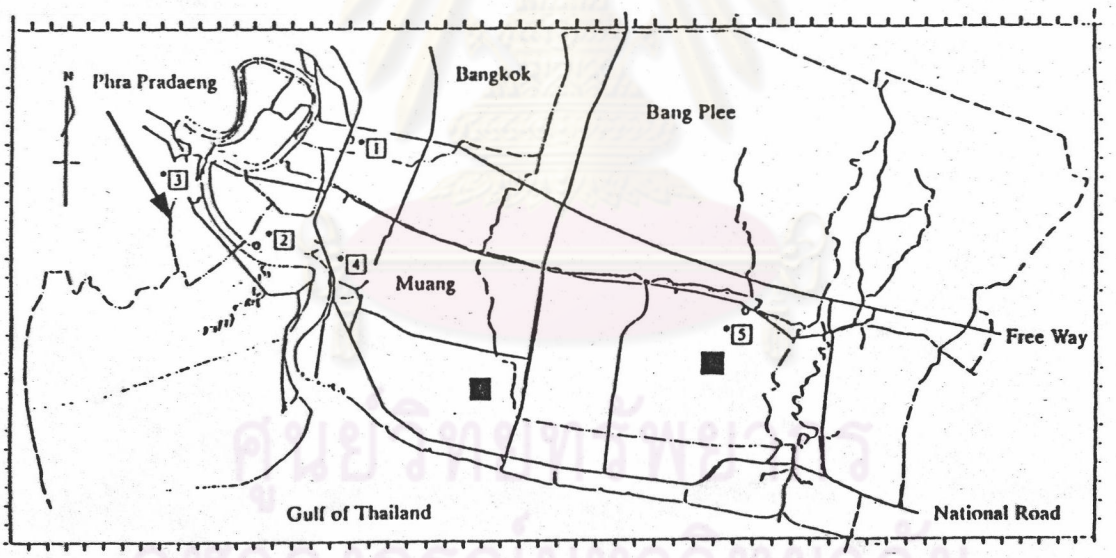

Figure 3.4 The Location of Survey Area

Table 3.3 Measured Sulfur Dioxide and Sulfate Concentrations in Bang Na (JICA, 1990)

Wind velocity (m/s)	2
SO_2 (ppb)	8.4
SO_4^{2-} (ng/m^3)	4500
$SO_{2,reacted}$ (ppb)	1.15
%Yield	13.67

In mathematical model simulation, plume rise is computed by using Briggs (1969)'s Equation which is in the form as follows:

$$\Delta h = \frac{1.6}{\bar{u}} \frac{[g V_s d^2 (T_s - T_a)]^{\frac{1}{3}}}{[4T_s]^{\frac{1}{3}}} x^{\frac{2}{3}} \qquad (3.21)$$

where

Δh = plume rise; (m)

$\bar{u}$ = wind velocity at stack height; (m/s)

g = gravitational acceleration; (m/s^2)

V_s = stack gas exit velocity; (m/s)

d = stack diameter; (m)

T_s = absolute flue gas exit temperature; (K)

T_a = absolute temperature of ambient atmosphere; (K)

x = downwind distance from source; (m)

As mentioned earlier, the program of mathematical model of sulfur dioxide oxidation in plume using the Monte Carlo method was written in C language and run on the Unix-based minicomputer at Chulalongkorn University Unix Center, Faculty of Engineering, Chulalongkorn University. Details of the programs are listed in Appendix A.

The results of the mathematical model simulations are presented in the form of %yield (percent of sulfate formation per sulfur dioxide emission) VS time. In ammonia-deficient environment case, sulfur dioxide, remaining ammonia and sulfate concentration profiles as functions of y and z distances are also shown.