Chapter IV

Results and Discussion

The results of the mathematical model simulations in accordance with the scope of study are separated into 4 parts as described below:

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

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

4.3   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

4.4   Evaluation of the simulated sulfate concentrations in comparison to the measured sulfate concentrations of a stack of the South Bangkok Power Plant in Samut Prakarn

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

The physical mathematical model, which is used to simulate the horizontal and vertical dispersion coefficients, shows that sulfur dioxide quanta at the end of run times are found to be accounted for all (100%) for every simulation.

The physico-chemical mathematical model, which is used to simulate the dispersion and chemical reaction, holds true on the mass conservation property for every condition of the simulation, that is:

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

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

The values of the simulated horizontal and vertical dispersion coefficients which make the under curve areas of the numerically calculated concentrations of sulfur dioxide nearly approach to the under curve areas of the empirical concentrations of sulfur dioxide as obtained by Gaussian equation using Pasquill-Gifford dispersion coefficients for every atmospheric stability class at 1, 5 and 10 km downwind from the source (except that for atmospheric stability class A and B at 5 and 10 km downwind, the plumes are so widely dispersed that evaluations were not possible.) are tabulated in Table 4.1.

From Table 4.1, the time step used in the numerical mathematical model for each atmospheric stability class is dependent on its wind velocity and the trajectory of each particle in the x direction which must be equal to 100 m during every time step. As a result the discrepancies of the empirical concentrations of sulfur dioxide in the unstable and neutral atmospheric stabilities for every 100 m in the y and z directions are considerably less than in the stable atmospheric stability (see Figure 4.1-4.14) and the greater number of sulfur dioxide quanta used in the same mass of sulfur dioxide, the smaller ratio of sulfur dioxide mass (g) per quantum was obtained. So the number of sulfur dioxide quanta put into the numerical mathematical model in the unstable and neutral atmospheric conditions needs to be much more than in the stable atmospheric condition for simulating the numerical concentrations of sulfur dioxide.

We have not succeeded in determining Pasquill-Gifford vertical dispersion coefficients for atmospheric stability class A at 5 and 10 km downwind and atmospheric stability class B at 10 km downwind in Figure 2.2. Consequently, we did not simulate the dispersion coefficients in these cases.

Table 4.1 Comparison of Pasquill-Gifford Dispersion Coefficients and the
Simulated Horizontal and Vertical Dispersion Coefficients for Every
Atmospheric Stability Class at 1, 5 and 10 km Downwind from the
Source

Downwind Distance (km)	Horizontal and Vertical dispersion coefficients (m)				SO_2 emission rate (g/s)	Numerical run conditions (quanta/time step,s)
	Pasquill -Gifford		Simulated			
	σ_y	σ_z	K_y	K_z		
For Class A						
1	215	590	45	147	500	1000/50
5	860	-	-	-	-	-
10	1600	-	-	-	-	-
For Class B						
1	160	130	25	17	500	1000/25
5	640	1850	-	-	-	-
10	1200	-	-	-	-	-
For Class C						
1	110	68	15	6.8	500	1000/20
5	450	250	43	13	500	2000/20
10	800	420	75	20	500	2000/20
For Class D						
1	75	31	4.65	0.05	500	1000/20
5	300	90	18	2.2	500	1000/20
10	550	150	41	2	500	2000/20
For Class E						
1	54	25	10	0.01	500	500/50
5	225	60	15	0.8	500	500/50
10	400	80	17	0.85	500	500/50
For Class F						
1	38	15	1.8	0	500	500/50
5	165	35	5	0.05	500	500/50
10	280	47	8.4	0.25	500	500/50

Due to the sysmetry of the plume, only a half of the plume is illustrated in Figure 4.1-4.14 and the details of each comparison are shown in Table 4.1. The under curve areas of the numerical concentration profiles that used the suitable simulated horizontal and vertical dispersion coefficients fit almost exactly with the under curve

areas of the empirical concentration profiles for every atmospheric stability class and downwind distance (except atmospheric stability class E and F at 1 km downwind) as shown in Figure 4.1-4.14. For atmospheric stability class E and F at 1 km downwind (see Figure 4.9 and 4.12), the under curve areas of the numerical concentration profiles differ greatly from the under curve areas of the empirical profiles due to the large volume of the center cells which prevents peaking as observed in empirical model.

In conclusion, the Monte Carlo dispersion model developed can satisfactorily simulate the dispersion of Pasquill-Gifford empirical model and thus can be used for the study of oxidation of sulfur dioxide in the plume in subsequent sections.

4.3 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

The results of studying sensitivity analysis of chemical reactions of physico-chemical mathematical model influencing sulfate formation by varying parameters such as atmospheric stability class, relative humidity, temperature, iron and ammonia concentrations in accordance with the types of chemical reactions are presented in 3 cases as below.

4.3.1 Brimblecombe and Spedding (1974)'s reaction rate

4.3.2 Freiberg (1974)'s reaction rate in ammonia-rich environment and in ammonia-deficient environment

4.3.3 Ibusuki, Ohsawa and Takeuchi (1990)'s reaction rate in ammonia-rich environment

4.3.1 Brimblecombe and Spedding (1974)'s Reaction Rate

We could not use Brimblecombe and Spedding (1974)'s reaction rate to evaluate the sulfate formation at both observed and high iron concentrations, because the rate constant is proportional to the iron concentration and depends upon pH in solution. The rate constant in Brimblecombe and Spedding (1974)'s reaction rate was established for the iron concentration of 10^{-6} M and pH of 4.9 but the observed and high iron concentrations are 2.15×10^{-11} and 1.79×10^{-9} M, respectively. It indicates that they are extremely dilute with respect to the experimental iron concentration (10^{-6} M). Thus, Brimblecombe and Spedding (1974)'s reaction rate should not be used to simulate the sulfate production for the given situations in Samut Prakarn.

4.3.2 Freiberg (1974)'s Reaction Rate in Ammonia-Rich Environment and in Ammonia-Deficient Environment

To minimize the number of variable parameters to be studied, every condition of Freiberg (1974)'s reaction rate in ammonia-rich environment was firstly simulated. Then the variable parameters, which strongly affect sulfate formation, were chosen to compute ammonia-deficient environment case.

The yields at any given time are demonstrated in Figure 4.15-4.46 and especially the yields at 10 km downwind in ammonia-rich environment and in ammonia-deficient environment are concluded in Table 4.2 and 4.3, respectively. The results of sensitivity analysis are discussed in the following subsections.

Table 4.2 Comparison of %Yield of Brimblecombe and Spedding (1974)'s Reaction Rate, Freiberg (1974)'s Reaction Rate and Ibusuki, Ohsawa and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment at 10 km Downwind from the Source

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m³)	[NH₃] (ppb)	T (°C)	%RH	%Yield
4.15-a)	2000	C	1201	50	20	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	0.85
4.15-b)	2000	C	1201	50	25	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	0.55
4.15-c)	2000	C	1201	50	30	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	0.3
4.16-a)	2000	C	1201	80	20	50	0.3
						70	0.3
						90	0.55
						95	0.25
						99	2.2
4.16-b)	2000	C	1201	80	25	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	0.75
4.16-c)	2000	C	1201	80	30	50	0.3
						70	0.3
						90	0.3

Table 4.2 Comparison of %Yield of Brimblecombe and Spedding (1974)'s
Reaction Rate, Freiberg (1974)'s Reaction Rate and Ibusuki, Ohsawa
and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment at
10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m^3)	[NH$_3$] (ppb)	T (°C)	%RH	%Yield
4.16-c)	2000	C	1201	80	30	95	0.3
						99	0.25
4.17-a)	2000	C	1201	100	20	50	0.3
						70	0.3
						90	0.3
						95	0.25
						99	4.7
4.17-b)	2000	C	1201	100	25	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	0.95
4.17-c)	2000	C	1201	100	30	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	0.55
4.18-a)	2000	C	0.1x10^6	50	20	50	0.3
						70	0.3
						90	0.25
						95	0.7
						99	30.25
4.18-b)	2000	C	0.1x10^6	50	25	50	0.3
						70	0.3
						90	0.3
						95	0.4
						99	6.9
4.18-c)	2000	C	0.1x10^6	50	30	50	0.3

Table 4.2 Comparison of %Yield of Brimblecombe and Spedding (1974)'s

Reaction Rate, Freiberg (1974)'s Reaction Rate and Ibusuki, Ohsawa

and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment at

10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m³)	[NH₃] (ppb)	T (°C)	%RH	%Yield
4.18-c)	2000	C	0.1×10^6	50	30	70	0.3
						90	0.3
						95	0.3
						99	1.15
4.19-a)	2000	C	0.1×10^6	80	20	50	0.3
						70	0.3
						90	0.55
						95	1.45
						99	75.05
4.19-b)	2000	C	0.1×10^6	80	25	50	0.3
						70	0.3
						90	0.25
						95	0.4
						99	22.45
4.19-c)	2000	C	0.1×10^6	80	30	50	0.3
						70	0.3
						90	0.3
						95	0.25
						99	3.75
4.20-a)	2000	C	0.1×10^6	100	20	50	0.3
						70	0.3
						90	0.7
						95	2.9
						99	87.55
4.20-b)	2000	C	0.1×10^6	100	25	50	0.3
						70	0.3
						90	0.4
						95	0.85

Table 4.2 Comparison of %Yield of Brimblecombe and Spedding (1974)'s Reaction Rate, Freiberg (1974)'s Reaction Rate and Ibusuki, Ohsawa and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment at 10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m^3)	[NH$_3$] (ppb)	T (°C)	%RH	%Yield
4.20-b)	2000	C	0.1x10^6	100	25	99	37.05
4.20-c)	2000	C	0.1x10^6	100	30	50	0.3
						70	0.3
						90	0.3
						95	0.4
						99	6.9
4.21-a)	2000	D	1201	50	20	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	1.4
4.21-b)	2000	D	1201	50	25	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	0.4
4.21-c)	2000	D	1201	50	30	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	0.3
4.22-a)	2000	D	1201	80	20	50	0.3
						70	0.3
						90	0.3
						95	0.25
						99	4.8
4.22-b)	2000	D	1201	80	25	50	0.3
						70	0.3

Table 4.2 Comparison of %Yield of Brimblecombe and Spedding (1974)'s

Reaction Rate, Freiberg (1974)'s Reaction Rate and Ibusuki, Ohsawa

and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment at

10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m^3)	[NH$_3$] (ppb)	T (°C)	%RH	%Yield
4.22-b)	2000	D	1201	80	25	90	0.3
						95	0.3
						99	1.15
4.22-c)	2000	D	1201	80	30	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	0.25
4.23-a)	2000	D	1201	100	20	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	9.4
4.23-b)	2000	D	1201	100	25	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	2.15
4.23-c)	2000	D	1201	100	30	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	0.4
4.24-a)	2000	D	0.1×10^6	50	20	50	0.3
						70	0.3
						90	0.25
						95	1.15
						99	50.6

Table 4.2 Comparison of %Yield of Brimblecombe and Spedding (1974)'s Reaction Rate, Freiberg (1974)'s Reaction Rate and Ibusuki, Ohsawa and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment at 10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m^3)	$[NH_3]$ (ppb)	T (°C)	%RH	%Yield
4.24-b)	2000	D	$0.1x10^6$	50	25	50	0.3
						70	0.3
						90	0.3
						95	0.4
						99	14.3
4.24-c)	2000	D	$0.1x10^6$	50	30	50	0.3
						70	0.3
						90	0.3
						95	0.3
						99	2.55
4.25-a)	2000	D	$0.1x10^6$	80	20	50	0.3
						70	0.3
						90	0.65
						95	3.7
						99	84.15
4.25-b)	2000	D	$0.1x10^6$	80	25	50	0.3
						70	0.3
						90	0.25
						95	0.55
						99	38.65
4.25-c)	2000	D	$0.1x10^6$	80	30	50	0.3
						70	0.3
						90	0.3
						95	0.55
						99	8.05
4.26-a)	2000	D	$0.1x10^6$	100	20	50	0.3
						70	0.3
						90	1.15

Table 4.2 Comparison of %Yield of Brimblecombe and Spedding (1974)'s

Reaction Rate, Freiberg (1974)'s Reaction Rate and Ibusuki, Ohsawa

and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment at

10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m^3)	[NH$_3$] (ppb)	T (°C)	%RH	%Yield
4.26-a)	2000	D	0.1x10^6	100	20	95	6.4
						99	91.6
4.26-b)	2000	D	0.1x10^6	100	25	50	0.3
						70	0.3
						90	0.4
						95	0.95
						99	57.55
4.26-c)	2000	D	0.1x10^6	100	30	50	0.3
						70	0.3
						90	0.4
						95	0.95
						99	14.85
4.27-a)	5000	E	1201	50	20	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	11.6
4.27-b)	5000	E	1201	50	25	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	3.8
4.27-c)	5000	E	1201	50	30	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	1
4.28-a)	5000	E	1201	80	20	50	0.4

Table 4.2 Comparison of %Yield of Brimblecombe and Spedding (1974)'s

Reaction Rate, Freiberg (1974)'s Reaction Rate and Ibusuki, Ohsawa

and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment at

10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m³)	[NH₃] (ppb)	T (°C)	%RH	%Yield
4.28-a)	5000	E	1201	80	20	70	0.4
						90	0.4
						95	1
						99	37.8
4.28-b)	5000	E	1201	80	25	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	6.6
4.28-c)	5000	E	1201	80	30	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	1.8
4.29-a)	5000	E	1201	100	20	50	0.4
						70	0.4
						90	0.4
						95	1
						99	51.2
4.29-b)	5000	E	1201	100	25	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	14.4
4.29-c)	5000	E	1201	100	30	50	0.4
						70	0.4
						90	0.4
						95	0.4

Table 4.2 Comparison of %Yield of Brimblecombe and Spedding (1974)'s

Reaction Rate, Freiberg (1974)'s Reaction Rate and Ibusuki, Ohsawa

and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment at

10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m³)	[NH₃] (ppb)	T (°C)	%RH	%Yield
4.29-c)	5000	E	1201	100	30	99	3.8
4.30-a)	5000	E	0.1×10^6	50	20	50	0.4
						70	0.4
						90	1.8
						95	6.6
						99	92.8
4.30-b)	5000	E	0.1×10^6	50	25	50	0.4
						70	0.4
						90	0.4
						95	1.8
						99	63.6
4.30-c)	5000	E	0.1×10^6	50	30	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	17
4.31-a)	5000	E	0.1×10^6	80	20	50	0.4
						70	0.4
						90	4.8
						95	27.4
						99	98.8
4.31-b)	5000	E	0.1×10^6	80	25	50	0.4
						70	0.4
						90	1
						95	6.4
						99	90.8
4.31-c)	5000	E	0.1×10^6	80	30	50	0.4
						70	0.4

Table 4.2 Comparison of %Yield of Brimblecombe and Spedding (1974)'s

Reaction Rate, Freiberg (1974)'s Reaction Rate and Ibusuki, Ohsawa

and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment at

10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m³)	[NH_3] (ppb)	T (°C)	%RH	%Yield
4.31-c)	5000	E	$0.1x10^6$	80	30	90	0.4
						95	1
						99	47.2
4.32-a)	5000	E	$0.1x10^6$	100	20	50	0.4
						70	1
						90	6.6
						95	44
						99	100
4.32-b)	5000	E	$0.1x10^6$	100	25	50	0.4
						70	1
						90	1.8
						95	8.8
						99	95.2
4.32-c)	5000	E	$0.1x10^6$	100	30	50	0.4
						70	0.4
						90	0.4
						95	1.8
						99	65.8
4.33-a)	5000	F	1201	50	20	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	4.8
4.33-b)	5000	F	1201	50	25	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	4.8

Table 4.2 Comparison of %Yield of Brimblecombe and Spedding (1974)'s
Reaction Rate, Freiberg (1974)'s Reaction Rate and Ibusuki, Ohsawa
and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment at
10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m³)	[NH₃] (ppb)	T (°C)	%RH	%Yield
4.33-c)	5000	F	1201	50	30	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	1
4.34-a)	5000	F	1201	80	20	50	0.4
						70	0.4
						90	0.4
						95	1.4
						99	49
4.34-b)	5000	F	1201	80	25	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	12.6
4.34-c)	5000	F	1201	80	30	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	2.8
4.35-a)	5000	F	1201	100	20	50	0.4
						70	0.4
						90	0.4
						95	1.6
						99	65.6
4.35-b)	5000	F	1201	100	25	50	0.4
						70	0.4
						90	0.4

Table 4.2 Comparison of %Yield of Brimblecombe and Spedding (1974)'s Reaction Rate, Freiberg (1974)'s Reaction Rate and Ibusuki, Ohsawa and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment at 10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m³)	[NH₃] (ppb)	T (°C)	%RH	%Yield
4.35-b)	5000	F	1201	100	25	95	0.4
						99	22.6
4.35-c)	5000	F	1201	100	30	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	4
4.36-a)	5000	F	0.1x10⁶	50	20	50	0.4
						70	0.4
						90	2.6
						95	15.2
						99	96
4.36-b)	5000	F	0.1x10⁶	50	25	50	0.4
						70	0.4
						90	0.4
						95	4.4
						99	72.6
4.36-c)	5000	F	0.1x10⁶	50	30	50	0.4
						70	0.4
						90	0.4
						95	0.4
						99	31.4
4.37-a)	5000	F	0.1x10⁶	80	20	50	0.4
						70	0.4
						90	10.4
						95	39.4
						99	99
4.37-b)	5000	F	0.1x10⁶	80	25	50	0.4

Table 4.2 Comparison of %Yield of Brimblecombe and Spedding (1974)'s
Reaction Rate, Freiberg (1974)'s Reaction Rate and Ibusuki, Ohsawa
and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment at
10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m^3)	[NH$_3$] (ppb)	T (^{o}C)	%RH	%Yield
4.37-b)	5000	F	0.1x10^6	80	25	70	0.4
						90	0.8
						95	11.4
						99	93.2
4.37-c)	5000	F	0.1x10^6	80	30	50	0.4
						70	0.4
						90	0.4
						95	1.6
						99	58.2
4.38-a)	5000	F	0.1x10^6	100	20	50	0.4
						70	1
						90	15.2
						95	52.6
						99	100
4.38-b)	5000	F	0.1x10^6	100	25	50	0.4
						70	0.4
						90	4.4
						95	18
						99	98.2
4.38-c)	5000	F	0.1x10^6	100	30	50	0.4
						70	0.4
						90	0.4
						95	4.4
						99	78

Remarks :

• No yields occur for Brimblecombe and Spedding (1974)'s reaction rate.

• For Ibusuki et al. (1990)'s reaction rate in ammonia-rich environment, there are %yield of 0.3 occurring in atmosphere stability class C and D and %yield of 0.4 occurring in atmospheric stability class E and F for every condition.

Table 4.3 %Yield of Freiberg (1974)'s Reaction Rate in Ammonia-Deficient
Environment at 10 km Downwind from the Source

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m³)	[NH₃] (ppb)	T (°C)	%RH	%Yield
4.39-a)	2000	C	1201	50	20	99	0.85
					25		0.45
					30		0.3
4.39-b)	2000	C	1201	80	20	99	2.3
					25		0.8
					30		0.6
4.39-c)	2000	C	1201	100	20	99	4.2
					25		0.75
					30		0.45
4.40-a)	2000	C	0.1×10^6	50	20	99	21
					25		5.95
					30		1.15
4.40-b)	2000	C	0.1×10^6	80	20	99	46.2
					25		17.25
					30		3.8
4.40-c)	2000	C	0.1×10^6	100	20	99	61.85
					25		28.9
					30		6.15
4.41-a)	2000	D	1201	50	20	99	1.3
					25		0.55
					30		0.3
4.41-b)	2000	D	1201	80	20	99	4.35
					25		1.2
					30		0.55
4.41-c)	2000	D	1201	100	20	99	7.55
					25		1.4
					30		0.55
4.42-a)	2000	D	0.1×10^6	50	20	99	27
					25		9.45
					30		2.6

Table 4.3 %Yield of Freiberg (1974)'s Reaction Rate in Ammonia-Deficient
Environment at 10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m³)	[NH₃] (ppb)	T (°C)	%RH	%Yield
4.42-b)	2000	D	0.1×10^6	80	20	99	54.5
					25		26.45
					30		7.35
4.42-c)	2000	D	0.1×10^6	100	20	99	67.5
					25		36.8
					30		12.05
4.43-a)	5000	E	1201	50	20	99	5.6
					25		2.4
					30		0.8
4.43-b)	5000	E	1201	80	20	99	15.2
					25		5.8
					30		2.4
4.43-c)	5000	E	1201	100	20	99	22.6
					25		8.2
					30		2.4
4.44-a)	5000	E	0.1×10^6	50	20	99	33.8
					25		19.2
					30		7.2
4.44-b)	5000	E	0.1×10^6	80	20	99	58.2
					25		37.4
					30		19.8
4.44-c)	5000	E	0.1×10^6	100	20	99	71
					25		49
					30		27.2
4.45-a)	5000	F	1201	50	20	99	6.2
					25		2.4
					30		0.6
4.45-b)	5000	F	1201	80	20	99	12.2
					25		5.6
					30		2.4

Table 4.3 %Yield of Freiberg (1974)'s Reaction Rate in Ammonia-Deficient

Environment at 10 km Downwind from the Source (Continued)

Figure	Time (sec)	Atmospheric Stability Class	[Fe] (ng/m³)	[NH₃] (ppb)	T (°C)	%RH	%Yield
4.45-c)	5000	F	1201	100	20	99	17.8
					25		9.2
					30		3
4.46-a)	5000	F	0.1x10⁶	50	20	99	22
					25		16.8
					30		6.8
4.46-b)	5000	F	0.1x10⁶	80	20	99	37.8
					25		27.6
					30		15.6
4.46-c)	5000	F	0.1x10⁶	100	20	99	44.8
					25		36
					30		21.4

4.3.2.1 Effect of Relative Humidity on %Yield

As shown in Figure 4.15-4.38, only 99% relative humidity significantly causes sulfate formation (%yield) for ammonia-rich environment, every atmospheric stability class, temperature and ammonia concentration at either observed iron concentration (1201 ng/m³) or high iron concentration (0.1 mg/m³) in heavily polluted atmosphere. Relative humidity in the range 50%-95% has no effect on iron-catalyzed oxidation of sulfur dioxide in aqueous phase for any given condition except that for stable atmospheric stability, high iron concentration and every ammonia concentration at temperature of 20 °C and 25 °C with relative humidity of 95% is of importance on sulfate formation (see Figure 4.30-4.32 and 4.36-4.38). The reasons why sulfate formation resulting from 99% relative humidity is much more than that resulting from relative humidity in the range 50%-95% are described as follows: As the relative humidity increases, the vapor pressure lowering of water on the droplet decreases below that of the surrounding atmosphere and induces more water to condense on the droplet.   As a result of the addition of water condensation in the droplet, the sulfuric acid concentration diminishes and pH rises.   The solubility of sulfur dioxide increases greatly with increasing pH.   So sulfur dioxide dissolves much more substantially into the drop while the relative humidity increases and more sulfur dioxide oxidation in aqueous phase occurs in order to maintain absorption equilibria of sulfur dioxide in water as constant.   Clearly, when the relative humidity increases from 50% to 70%, from 50% to 90%, from 50% to 95% and from 50% to 99%, the amount of condensed water increases 1.67-fold, 5-fold, 10-fold and 50-fold, respectively. Accordingly high relative humidity considerably influences the catalytic oxidation of sulfur dioxide in aqueous phase.

Only relative humidity of 99% plays a significant role in sulfur dioxide oxidation in aqueous phase for every condition of ammonia-rich environment.   So it is

selected to study simultaneously with other parameters for ammonia-deficient environment case.

4.3.2.2 Effect of Temperature on %Yield

As temperature increases, the yield of the catalytic oxidation of sulfur dioxide decreases in both of ammonia-rich environment and ammonia-deficient environment as demonstrated in Figure 4.15-4.46. As a result the value of $K_o*\beta_s^2*K_s^2*\beta_n^3*K_n^3/K_w^3$ reduces approximately by 84%-89% for every temperature increase of 5 °C. Thus, the temperature increase affects mainly the decrease in the sulfur dioxide to sulfate transformation.

At 99% relative humidity in ammonia-rich environment and in ammonia-deficient environment, %yield is considerably different for every temperature increment of 5 °C. But at relative humidity in the range 50%-95% in ammonia-rich environment except for the stable atmospheric stability, high iron concentration and every ammonia concentration, %yield has a very small discrepancy for every temperature change of 5 °C. The results here show that the sensitivity of %yield to temperature depends mainly on relative humidity. In conclusion, there is a maximum %yield at the highest relative humidity and lowest temperature for the same atmospheric condition.

4.3.2.3 Effect of Iron Concentration on %Yield

The results as depicted in Figure 4.47-4.54 are discussed as follows: %Yield is extremely diminutive (mostly less than 2% and not over 10%) in ammonia-rich environment and in ammonia-deficient environment for the unstable and neutral atmospheric stabilities at observed iron concentration, 99% relative humidity, temperature and ammonia concentration variations. On the other hand, %yield is large not only in ammonia-rich environment but also in ammonia-deficient environment for the stable atmospheric stability and at the lower temperature. The conclusion here is that in Samut Prakarn, observed iron concentration influences markedly on sulfate

formation in the stable atmospheric stability at relative humidity of 99%, temperature of 20 °C and ammonia variations, particularly in ammonia-rich environment. When iron concentration rises from 1201ng/m^3 to 0.1 mg/m^3, %yield catalyzed by high iron concentration is much greater for every atmospheric stability condition. Therefore, the amount of iron concentration is essential for the iron catalyzed oxidation of sulfur dioxide in solution.

4.3.2.4 Effect of Ammonia Concentration on %Yield

Yield keeps increasing while the ammonia concentration increases from 50 ppb to 80 ppb or to 100 ppb in both ammonia-rich environment and ammonia-deficient environment as presented in Figure 4.47-4.54. The results here can be elucidated as follows: Sulfate aerosol produced by the catalytic oxidation of sulfur dioxide in aqueous phase causes the lowering of the pH. The rate of the heterogeneous of sulfur dioxide oxidation is limited by acidification in solution. Consequently, the solubility of sulfur dioxide increases with an increasing pH. Accordingly, to keep the sulfur dioxide oxidation continuing, the acidity must be neutralized and buffered by the ammonia concentration. The higher ammonia concentration, the higher increase in the acid neutralizing buffer capacity to counteract the acidity generated from the sulfur dioxide oxidation. Therefore, the amount of ammonia concentration regulates the extent of the iron-catalyzed oxidation of sulfur dioxide.

Most of the %yield in ammonia-rich environment is much more than that in ammonia-deficient environment for the same given condition as portrayed in Figure 4.47-4.54 because the acid neutralizing buffer capacity of the ammonia availability in ammonia-rich environment is much higher than that in ammonia-deficient environment. The ammonia concentration in the first condition was assumed to be constant, but the ammonia concentration in the latter condition is depleted by neutralizing the acid formed by sulfur dioxide oxidation as long as all ammonia concentration is not exhausted.

There is no difference of %yield between in ammonia-rich environment and in ammonia-deficient environment for some given condition, meaning that the acid neutralizing buffer capacity of ammonia concentration in ammonia-deficient environment is still enough to neutralize the acidity due to the sulfur dioxide oxidation and thus in turn there is some remaining ammonia concentration. This occurs on the unstable and neutral atmospheric conditions.

As demonstrated in Figure 4.55-4.56 for ammonia-deficient environment, sulfur dioxide concentration reduces from the plume center to the periphery of the plume as a consequence of dispersion. Remaining ammonia concentration shows an inverse Gaussian concentration profile versus sulfate concentration. Due to ammonia limitation, ammonia can not penetrate into the plume center. Thus, sulfate formation at the plume center is less. In conclusion, ammonia reacts with sulfate from the edge of the plume toward the center line. Freiberg (1974)'s reaction rate in ammonia-deficient environment thus is limited by ammonia concentration, not by sulfur dioxide concentration.

4.3.2.5 Effect of Atmospheric Stability Class on %Yield

For each atmospheric stability of any given condition as illustrated in Figure 4.47-4.54, yield is rapid in early plume life and then proceeds at a slower rate and mostly tends to converge toward a constant. The situation, which happens above, can be explained as follows: Sulfate formation is controlled by sulfur dioxide concentration. At the beginning of the plume life, sulfur dioxide concentration is high and subsequently lower due to the dilution of sulfur dioxide as a consequence of atmospheric dispersion. Accordingly, the heterogeneous oxidation of sulfur dioxide in an expanding plume continues to an asymptotic limit. This phenomenon has been discussed by Freiberg (1978).

The sulfate production is very low in the unstable and neutral atmospheric stabilities at observed iron concentration as shown in Figure 4.47 and 4.49 since the sulfur dioxide dispersion due to transportation with high wind velocity and diffusion by turbulent eddies and good mixing does not promote the second order sulfur dioxide oxidation rate. Vice versa, the conversion of sulfur dioxide to sulfate is very high in the stable atmospheric stability at observed iron concentration as represented in Figure 4.51 and 4.53 because the overall sulfur dioxide oxidation rate is high due to low wind velocity and poor mixing.

The yield for any given condition as depicted in Figure 4.47-4.54 indicates that the temperature decrease, the iron and ammonia concentration increase in each atmospheric stability class not only in ammonia-rich environment but also in ammonia-deficient environment cause the increment of the overall sulfur dioxide oxidation rate whereas the sulfur dioxide dispersion rate remains constant. So the ratio of the overall sulfur dioxide oxidation rate to the sulfur dioxide dispersion rate is essential for the conversion of sulfur dioxide to sulfate. If the overall sulfur dioxide oxidation rate is much larger than the sulfur dioxide dispersion rate, sulfate formation is high and may proceed to almost completion. On the contrary, if the sulfur dioxide dispersion rate is much greater than the overall sulfur dioxide oxidation rate, sulfate production is low and may result in very slow reaction.

4.3.3 Ibusuki, Ohsawa and Takeuchi (1990)'s Reaction Rate in Ammonia-Rich Environment

Ibusuki et al. (1990)'s reaction rate does not cause significant yield as shown in Table 4.2 for each atmospheric stability class, nor as a result of the temperature decrease or the relative humidity increase or the ammonia concentration increase or iron concentration increase. The hydrogen ion concentration, which is related to the relative humidity and the ammonia concentration, and the iron concentration in Ibusuki et al (1990)'s reaction rate increase with the exponent 0.5 which produce very small

rate constant for any condition. So there is no difference in the probability of sulfur dioxide to sulfate transformation of each sulfur dioxide quantum due to the relative humidity or iron concentration or ammonia concentration variations.

4.4 Evaluation of Simulated Sulfate Concentrations in Comparison to Measured Sulfate Concentrations of a Stack of the South Bangkok Power Plant in Samut Prakarn

The comparison of measured yield, Freiberg's yields and Alkezweeny and Powell's yield are concluded in Table 4.4.

Table 4.4 Comparison of Measured Yield, Freiberg's Yields and Alkezweeny and Powell's Yield at Temperature of 25 °C and 7 km Downwind from the Source

Wind velocity (m/s)	%Yield					
	measured	Freiberg				Alkezweeny and Powell
		#1	#2	#3	#4	
2	13.67	12.6	20.8	7.4	7.8	4.85

#1 : For atmospheric stability class E in ammonia-rich environment at RH of 99%, [Fe] = 1201 ng/m³ and [NH₃] = 100 ppb

#1 : For atmospheric stability class E in ammonia-rich environment at RH of 99%, [Fe] = 1201 ng/m^3 and [NH_3] = 100 ppb

#2 : For atmospheric stability class F in ammonia-rich environment at RH of 99%, [Fe] = 1201 ng/m^3 and [NH_3] = 100 ppb

#3 : For atmospheric stability class E in ammonia-deficient environment at RH of 99%, [Fe] = 1201 ng/m^3 and [NH_3] = 100 ppb

#4 : For atmospheric stability class F in ammonia-deficient environment at RH of 99%, [Fe] = 1201 ng/m^3 and [NH_3] = 100 ppb

The measured yield value (SO_4^{2-} /SO_2) as obtained by JICA (1990) was used to compare with the model results. Only the data obtained during the southeasterly monsoon of 1988 (since the wind direction must be from power plant towards the

measured location at Bang Na station (MS1)). It is found that during the dry season of 1988, the SO_4^{2-}/SO_2 is 13.67% yield, where Alkezweeny and Powell (1977)'s reaction rate gives the yield of 4.85% at the location of MS1 with wind velocity of 2 m/s. Freiberg (1974)'s reaction rate in many cases provide the yields of 7.4-20.8%. Since in the dry season it is very much likely that relative humidity is below 90% most of the time, the contribution of Freiberg (1974)'s reaction rate toward the yield may not be very significant .

The observation of such high SO_4^{2-}/SO_2 ratio by JICA (1990) can be explained by at least two mechanism: One is the oxidation at source ($SO_2 \rightarrow SO_3$ in gas phase at high temperature and excess oxygen with catalytic reactions , i.e. vanadium and manganese) which has been known to contribute to sulfate formation. The other reason is the fuel that sulfur dioxide is emitted from other small sources which may have different SO_4^{2-}/SO_2 ratio than EGAT's.

However, the heterogeneous gas phase oxidation of sulfur dioxide according to Freiberg (1974)'s reaction rate can be an important mechanism if the atmospheric condition is right, as in certain case, i.e. #1 and #2. The yields can be as high as 12.6-20.8% which is close to or over the observed concentration.