OCD0--9700/488

Project Number: OCRC/4.10
Project Title: The Effect of Additives on Lime Dissolution Rates
Name of Grantee:
Address: Civil & Environmental Engineering Department
University of Cincinnati
Cincinnati, Ohio 45221
(513) 556-2518
Project Manager: Tim C. Keener
Period of Performance: November 1, 1994 - February 28, 1996

FINAL REPORT

This project was funded in part
by the Ohio Coal Development Office
Department of Development
State of Ohio

RECEIVED

JUL 25 1996

DEPARTMENT OF DEVELOPMENT
OHIO COAL DEV OFFICE

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Date: July 31, 1996
Other Investigators: S.J. Khang, CO-PI
J. Wang, Graduate Student

MASTER

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

EXECUTIVE SUMMARY

Spray drying processes have different physical and chemical features compared with wet scrubbing operations. The dissolution rates of lime and limestone could become a critical limiting step for desulfurization. Spray drying processes contain two phenomena that are totally different from wet scrubbing. One is the short residence time of the liquid phase in droplets, and the second are the highly concentrated ions in droplets and the ion interactions accompanying the water evaporation. According to the literature, the second phenomenon has a relationship to the lime dissolution rate, and because of these phenomena, the lime dissolution rate needs special considerations and studies. Since the dissolution rate can become the limiting step for the overall SO_2 removal in spray dryers (as seen from using different sorbents such as NaOH , Ca(OH)_2 , and CaCO_3), higher dissolution rate could mean higher sorbent utilization. Based on the above reasons, the objectives of this study were;

1. Conduct experiments to measure the dissolution rate of lime. Study the mechanisms of the sorbent (Ca(OH)_2) dissolution rates and the factors that have the greatest effects on the dissolution rate.
2. Study the influence of additives on lime dissolution rates. These additives may exist as trace compounds in the sorbents, the products of the SO_2 , or other gaseous pollutants reacted with the sorbents or added as artificial additives.
3. Incorporate these results into a predictive model which could be used to anticipate changes to performance from baseline conditions.

Six organic additives were tested for their effect on lime dissolution rate. These were phenol, sucrose, glycerin, ammonium acetate, urea, and ethyl-alcohol. For the three additives phenol, sucrose, and glycerin in the additive concentration range of less than 10% by weight, phenol has the greatest effect on lime dissolution rate. When phenol concentrations reach 20%, the lime dissolution rate declines because not all the phenol in water is dissolved. Sugar

enhances the dissolution rate of lime steadily. Adding glycerin to the solution seems to result in little improvement on lime dissolution over pure water, and an increase in glycerin concentration leads to no further improvement in the lime dissolution rate. For all the organic additives, ammonium acetate has the greatest effect in enhancing lime dissolution rate. Urea increase lime dissolution slightly. Alcohol decreased the lime dissolution rate.

Six inorganic additives were also tested for their effects on lime dissolution rate. They were NH_4Cl , NH_4NO_3 , NH_4I , $(\text{NH}_4)_2\text{SO}_4$, CaCl_2 , and NaCl . It was found that most ammonium inorganic compounds have the ability to increase lime dissolution rate. This phenomenon was first considered a chemical reaction, but the activation energy calculated from further tests on NH_4Cl dissolution rate versus temperature indicated that NH_4Cl accelerated the mass transfer process. With a 2% NH_4Cl weight concentration, the lime dissolution rate increased by almost 40 times. The experiment results also showed that ammonium sulfate does not give similar results on lime dissolution enhancement. Further studies found that the insignificant effect by ammonium sulfate is due to the lower solubility of calcium sulfate which could be deposited back onto the calcium hydroxide and prevent further dissolution into the solution.

In pilot plant tests, ammonium chloride as an additive to increase dissolution rate was found to increase SO_2 uptake significantly. Tests with 0.5% concentration addition of NH_4Cl to the slaked lime solution showed a 50% increase in SO_2 removal for a simulated high sulfur coal flue gas. The 0.5% concentration increase was estimated to increase the lime dissolution rate by a factor of two, indicating the sensitivity to SO_2 uptake to the lime dissolution rate.

The results of the bench scale and pilot scale tests on additives have been incorporated into a numerical predictive model called SPRAYMOD-M. This model is a comprehensive coupled heat and mass transfer description of the reaction mechanisms responsible for removal of SO_2 in spray dryers. The model has been modified to incorporate the results from these studies concerning the improvements in removal efficiency and dissolution rate via the use of additives. These effects include increased hygroscopicity and enhanced dissolution of the parent calcium hydroxide particles into the slurry water.

TABLE OF CONTENTS

EXECUTIVE SUMMARY	i
CHAPTER 1: INTRODUCTION	1
CHAPTER 2: EFFECT OF SLAKING PARAMETERS ON LIME DISSOLUTION RATE ..	3
CHAPTER 3: THE EFFECT OF ADDITIVES ON LIME DISSOLUTION RATE	7
CHAPTER 4: PILOT SCALE VERIFICATION OF THE EFFECT OF INORGANIC ADDITIVES ON THE DISSOLUTION RATE AND SO ₂ UPTAKE EFFICIENCY ..	19
CHAPTER 5: THE EFFECT OF NH ₄ CL ON LIMESTONE DISSOLUTION	23
CHAPTER 6: SPRAY DRYER MODELING	26
Introduction to "SPRAYMOD-M"	26
Drying Processes	27
The Constant Rate Period	27
The Falling Rate Period	31
SO ₂ Absorption Process	32
Constant Rate Period:	32
Falling Rate Period	34
Derivation of Simplified Model for SO ₂ Removal in Spray Dryer	34
Application of "SPRAYMOD-M" on Baseline Test Results	38
Modification of "SPRAYMOD-M" for Hygroscopic Additive Effects	39
The Mechanism of Hygroscopicity	39
The Mechanisms of Dissolution Rate Enhancing Additives	42

CHAPTER 7: CONCLUSIONS	57
REFERENCES	59
APPENDIX	60
Appendix A: Additive Effects Applied to "SPRAYMOD-M"	60
Appendix B: List of the Meaning of Code Variables in SPRAYMOD-M	82

LIST OF TABLES

Table 1-1. Results of Freshly Slaked Lime Dissolution Rate	5
Table 3-1. Results of Lime Dissolution Rate Effected by Organic Additives	11
Table 3-2. Solubilities of Calcium Compounds by Replacing Ammonium Ion with Calcium Ion From the Ammonium Compounds	12
Table 3-3. Results of Lime Dissolution Rate Effected by Inorganic Additives	13
Table 5-1. Comparison of Results for F2-14 Limestone Dissolution Rate in Different Conditions	24
Table 6-1. SPRAYMOD-M Operating Parameters and Standard Conditions	43
Table 6-2. Solubilities of Ca^{2+} and Na^{+} Substances	44
Table 6-3. Comparison of the im/M_s term for different substances	44

LIST OF FIGURES

Figure 1-1. Slaked Lime Quality as Affected by Water:CaO Ratio and Water Temperature	6
Figure 3-1. Lime Dissolution Rate Under Different Additive Solutions as a Function of Additive Concentrations.	14

Figure 3-2. Lime Dissolution Rate Effected by Ammonium Compounds.	15
Figure 3-3. Lime Dissolution Rate versus Temperature as Derived From Activation Energy Formula.	16
Figure 3-4. Measured Solution pH versus Time for Lime Dissolution Without Additives.	17
Figure 3-5. Measured Solution pH versus Time for Lime Dissolution With 2% NH_4Cl	18
Figure 4-1. Real Time SO_2 Removal Efficiency Across Spray Dryer and Spray Dryer Outlet Temperature versus Time (Baseline)	20
Figure 4-2. Real Time SO_2 Removal Efficiency Across Spray Dryer and Approach to Saturation Temperature versus Time (With NH_4Cl).	21
Figure 4-3. Plot of SO_2 Removal versus Lime Dissolution Rate for Experimental Results from Pilot Plant Testing.	22
Figure 5-1. F2-14 Limestone Dissolution Rate versus Different NH_4Cl Concentration at Room Temperature and pH Upper Limit 5.40.	25
Figure 6-1. Schematic Diagram for SO_2 Absorption into Slurry Droplets.	45
Figure 6-2. Schematic Drawing for Derivation of Spray Dryer Desulfurization Model.	46
Figure 6-3. SO_2 Removal versus Ca/S Molar Ratio for Baseline $\text{Ca}(\text{OH})_2$	47
Figure 6-4. Baseline SO_2 Removal versus Approach to Saturation Temperature.	48
Figure 6-5. $\text{Ca}(\text{OH})_2$ Particle Size Distribution Measured by Coulter Counter.	49
Figure 6-6. Baseline SO_2 Removal versus Approach to Saturation Temperature.	50
Figure 6-7. Water Vapor Partial Pressure Over NaOH Solution Plane Surface.	51
Figure 6-8. Ratio of Pressure of Droplet Surface to Plane Pure Water Surface versus Droplet Size	52
Figure 6-9. Comparison of Model Prediction and Experimental Data on SO_2 Removal versus Approach to Saturation Temperature.	53
Figure 6-10. Comparison of Model Prediction and Experimental Data on SO_2 Removal versus Approach to Saturation Temperature.	54
Figure 6-11. SO_2 Removal and Spray Dryer Outlet Temperature Continuous Monitoring as Compared to Model Prediction (Baseline).	55
Figure 6-12. SO_2 Removal and Approach to Saturation Temperature Continuous Monitoring and	

Model Prediction (0.5% NH ₄ Cl).	56
---	----

CHAPTER 1: INTRODUCTION

Based on the previous years' studies concerning the efficiency of SO₂ removal by spray dryers with high sulfur coal flue gas, the work for year five included investigations of lime dissolution rates at different slaking conditions and with the effect of additives. The prominent additives that have significant effects on lime dissolution rates were tested with the mini pilot spray drying absorber to see their effects on spray drying desulfurization applications. The mechanisms of these additive effects along with the properties of hygroscopic additives have been discussed and incorporated into the spray drying desulfurization model "SPRAYMOD-M."

Slaking conditions are very important factors in producing high quality lime slurry in spray drying desulfurization processes. At optimal slaking conditions, the slaked lime particles are very fine (3-5um) and the slaked lime has high BET surface areas which are beneficial to the desulfurization. The high specific surface area indicates that for a given mass of lime, more lime can dissolve into the lime solution in a unit time. The slaked lime dissolution rate experiments in our study are designed to determine how much lime can dissolve in a unit time if the initial lime surface area is kept constant.

The purpose of the dissolution rate study for different additives is to find those effective additives that can enhance lime dissolution rates and to investigate the mechanisms of the dissolution rate enhancement properties for these additives. The applications of these additives on spray drying desulfurization are to further verify the theory that dissolution rate is a rate limiting step in the whole spray drying desulfurization process as well as to test the feasibility of these additives on enhancing SO₂ removal in spray dryers.

The modification of "SPRAYMOD-M" has been accomplished in order to integrate the additive effects into an established mathematical model. There are two kinds of additives that were found to be effective in enhancing SO₂ removal in spray dryers. One is in the hygroscopic category and another is in the dissolution rate category. The hygroscopic additive properties are incorporated into the model through the lowering of the water vapor pressure on the droplet surface, i.e., lowering the water vapor evaporation driving force. The dissolution rate enhancing properties are incorporated into the model through the lime dissolution film thickness in the original model.

CHAPTER 2: EFFECT OF SLAKING PARAMETERS ON LIME DISSOLUTION RATE

In the lime viscosity reduction test, Shelly et al. (Shelly, D.P. et al, 1983) has derived expressions for comparing slurry reactivity. Reactivity was estimated as quality (Q), and approximations of the available alkalinity of the slaked lime expressed as available lime. In the derivation of the expression, two assumptions were made: (1) grits and inerts are defined as all +100 mesh particles that are not available CaO; (2) all slaked lime particles smaller than 100 mesh are $\text{Ca}(\text{OH})_2$. The expression for slaked lime quality is given in equation 1.

$$Q = 1 - \frac{(\text{Grams of } +100 \text{ Mesh}) - (\text{Grams of CaO } \in +100 \text{ Mesh})}{(\text{Grams of quicklime feed})} \quad (1)$$

Slaking experiments were performed with CaO supplied by Dravo Lime Company and tap water to determine the effect of slaking conditions on lime quality. The quality of lime in terms of the slaking water temperature is shown in Figure 1-1. Lime quality was found to be above ~95% for slaking conditions where the water temperature was equal-to-or-greater-than 20°C, and the water to lime ratios were less than seven.

In a series of slaked lime dissolution tests, the dissolution rate of $\text{Ca}(\text{OH})_2$ powders produced from different water:CaO ratios were studied. The fresh quicklime from Dravo Lime Company was slaked at different water:CaO ratios in the laboratory. The highest slaking temperature was measured. The slaked lime was then sieved through a 100-mesh screen to remove the grit (except for a water:CaO ratio of 3.11:1 which was too thick to flow), and the sieved slurry was then filtered to obtain lime filter cake. The filter cake was then dried in a vacuum desiccator at ~ 80° C. The dried lime filter cake was then broken into small pieces

(particle sizes less than 1/8") and pressed into disks as described in a previous project report (Keener et al, 1995). These disks were used for dissolution rate tests. The results are shown in Table I.

As shown in Table I, the maximum temperature obtained in the slaking process decreases as the slaking water:CaO ratio increases. The dissolution rate for 3.11:1 ratio slaked lime is a little lower than that at the other ratio because the grit in the slurry was not removed. From a ratio 4:1 to 5:1, the dissolution rate decreases as expected, but from 6:1 above, the dissolution rate increases. This increase above the ratio 6:1 is due to the hardness of the mortared particles. It was observed that the pressed disk from the material of the higher ratio slaked lime had more porosity; therefore, the higher dissolution rate is due to the porosity increase of the pressed disk. At a 4:1 ratio, the dissolution rate of slaked lime is approximately that of the analytical grade lime powder, which is 6.05 gmole/cm²-s at about 50°C. Therefore, the slaked lime dissolution rate does not exceed the dissolution rate of lime powder under the same experimental conditions.

Table 1-1. Results of Freshly Slaked Lime Dissolution Rate.

H ₂ O : CaO (by Weight)	Highest Slaking Temp, °F	pH Upper Limit	Average pH	Average Temperature, °C	Dissolution Rate x10 ⁸ gmole/cm ² -s
3.11 : 1	180	7.0	5.81	49.16	5.46
4.0 : 1	140	7.0	6.06	48.96	5.94
5.0 : 1	130	7.0	5.95	43.27	5.64
6.0 : 1	122	7.0	5.76	53.92	5.91
7.0 : 1	101	7.0	6.00	49.78	8.89
8.0 : 1	110	7.0	6.18	54.64	9.84

Figure 1-1. Slaked Lime Quality as Affected by Water:CaO Ratio and Water Temperature

CHAPTER 3: THE EFFECT OF ADDITIVES ON LIME DISSOLUTION RATE

From solubility studies, it has been found that most inorganic salts increase Ca(OH)_2 solubility by 10-15% in 0.1-0.2% salt solutions. But several soluble organic substances markedly increase Ca(OH)_2 solubility far greater than any inorganic chemicals. Glycerol at 25°C yields a steady increase in solubility up to a glycerol concentration of 69%. Ca(OH)_2 solubility at the maximum glycerol level is 3.55g $\text{CaO}/100\text{g}_{\text{H}_2\text{O}}$, which is about 22 times greater than Ca(OH)_2 solubility in pure water. Phenol produces an even greater rise in Ca(OH)_2 solubility. At 23°C and 30% phenol concentration, Ca(OH)_2 solubility can reach 8.67g $\text{CaO}/100\text{g}_{\text{H}_2\text{O}}$, which is an increase of 75 times over pure water. Sugar exerts the greatest influence on lime solubility. At 25°C and 35% sugar concentration, Ca(OH)_2 solubility can reach its maximum of 10.1g $\text{CaO}/100\text{g}_{\text{H}_2\text{O}}$, which is 100 times more than Ca(OH)_2 solubility in pure water (Boynton, 1980).

Six organic additives were tested for their effect on lime dissolution rate. These were phenol, sucrose, glycerin, ammonium acetate, urea, and ethyl-alcohol. For the three additives, phenol, sucrose, and glycerin, the dissolution rate of Ca(OH)_2 with respect to the additive concentration is shown in Figure 3-1. It can be seen in Figure 3-1 that for the additive concentration range less than 10% by weight, phenol has the greatest effect on lime dissolution rate. When phenol concentrations reach 20%, the lime dissolution rate declines because not all the phenol is dissolved in water. Sugar enhances the dissolution rate of lime steadily. Adding glycerin to the solution seems to result in little improvement on lime dissolution over pure water, and an increase in glycerin concentration leads to no further improvement in the lime dissolution rate. For all the organic additives, the test results are shown in Table 3-1 where it can be seen

that ammonium acetate has the greatest effect in enhancing lime dissolution rate. Urea increase lime dissolution slightly. Alcohol decreased the lime dissolution rate.

Six inorganic additives were also tested for their effects on lime dissolution rate. They were NH_4Cl , NH_4NO_3 , NH_4I , $(\text{NH}_4)_2\text{SO}_4$, CaCl_2 , and NaCl . It was found that most ammonium inorganic compounds have the ability to increase lime dissolution rate tremendously, as can be seen from Figure 3-2. This phenomenon was first considered a chemical reaction, but the activation energy calculated from further tests on NH_4Cl dissolution rate versus temperature indicated that NH_4Cl in some way accelerated the mass transfer process. With a 2% NH_4Cl weight concentration, the lime dissolution rates versus different temperatures are shown in Figure 3-3. The activation energy was calculated to be 3.63 kcal/g-mole, which is much less than that of a chemical reaction. The experiment results also showed that ammonium sulfate does not produce the same effect on lime dissolution. Further studies found that the insignificant effect by ammonium sulfate is due to the lower solubility of calcium sulfate which could be deposited back onto the disk surface to block further calcium hydroxide dissolution into the solution. Of the other ammonium compounds, all the calcium compounds formed by the anions and calcium ions have high solubilities. The solubilities of corresponding calcium compounds are shown in Table 3-2. The inorganic additive effects on lime dissolution rate are shown in Table 3-3.

The pH of the solution in the lime dissolution test with ammonium chloride did not change as greatly as for the case of lime dissolution without additives (both tests used the same concentration of HCl , 0.05N). This can be seen in Figure 3-4 and Figure 3-5. Figure 3-4 is the recorded pH of the solution without additives, and Figure 3-5 is the recorded pH of the solution

with 2% ammonium chloride concentration by weight. As can be seen in Figure 3-5, the solution pH stays very stable with the addition of ammonium. There are two possible ways to explain this phenomenon. One is that ammonium chloride makes the lime disk dissolve faster so that as soon as the acid is pumped into the solution it is neutralized. Another is that the hydrogen ions from the titration acid could combine with the dissolved NH_3 to form ammonium ions $\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$, thus keeping the solution pH more stable.

Both the ionic strength and the composition of solution affect the rate constant and equilibrium constant of lime dissolution. For the inorganic additives, since all the additives are electrolytes, adding these additives to the solution will change both the ionic strength and the composition of the solution.

Adding inorganic additives to the solution will increase the ionic strength which will reduce the activity coefficient for lime dissolution. This reduction of the activity coefficient will enable the lime dissolution equilibrium to move toward ionization (or dissolution). The additives thus will increase the potential (driving force) for lime dissolution or mass transfer into the solution. The higher the concentration of additives, the more the reduction of the activity coefficient, and thus the more Ca^{2+} and OH^- are demanded by the solution. This will explain why at higher additive concentrations the dissolution rate of lime has a higher value.

The rate constant and equilibrium constant are also influenced by the composition of the solution. This is why at 10% concentration the CaCl_2 and NaCl have different effects on lime dissolution.

In the case of ammonium compounds, the above theory will not be enough to explain the huge increase of lime dissolution rate. The following chemical processes will elucidate the

ammonium compound effects. For example, NH_4Cl , when in solution will ionize by the following equation $\text{NH}_4\text{Cl} \rightarrow \text{NH}_4^+ + \text{Cl}^-$. Lime will dissolve as $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$. The ammonium ion will combine with the hydroxyl ion as $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$, and this equilibrium will remove the hydroxyl ions in the solution and produce ammonia gas NH_3 . By this way, the hydroxyl ions in the solution will be kept at a lower level, which will enable the $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ to move toward the right-hand side. On the other hand, the Ca^{2+} ion will not combine with Cl^- ion to form a deposit because of the high solubility of the CaCl_2 ; on the contrary, the CaSO_4 has a low solubility and therefore the overall effect of $(\text{NH}_4)_2\text{SO}_4$ additive is not significant.

Little has been known about the mechanisms of the organic additive effects. Based on the calcium hydroxide dissolution $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$, the organic substance must have combined with either Ca^{2+} or OH^- to reduce the ion concentrations of Ca^{2+} or OH^- in order to make the equilibrium move toward the right-hand side.

Table 3-1. Results of Lime Dissolution Rate Effected by Organic Additives

Additive Name	Additive % Weight in Solution	pH Stat Upper Limit	Average pH of Solution	Average Temp of Solution °C	Dissolution Rate of Lime $\times 10^8$ gmol/cm ² -sec.
Pure Water	0%	7.00	6.49	49.04	6.05
Tap Water	0%	7.00	6.95	51.05	6.39
Sucrose	2%	7.00	6.21	55.52	7.11
	10%	7.00	6.61	51.68	13.86
	20%	7.00	7.18	48.63	37.19
Phenol	2%	7.00	6.71	50.75	12.58
	10%	7.00	6.91	46.99	34.99
	20%	7.00	6.91	44.24	31.07
Glycerin	2%	7.00	6.13	50.97	9.36
	10%	7.00	6.28	51.75	9.72
	20%	7.00	6.42	50.97	10.64
NH ₄ C ₂ H ₃ O ₂	2%	7.00	7.02	47.28	21.32
Urea	2%	7.00	4.52	45.60	7.52
Alcohol	10%	7.00	5.89	54.12	4.98

Table 3-2. Solubilities of Calcium Compounds by Replacing Ammonium Ion with Calcium Ion From the Ammonium Compounds [Perry's Chemical Engineers' Handbook]

Name	0°C	10°C	20°C	30°C	40°C	50°C	60°C	70°C	80°C	90°C	100C
Acetate .2H ₂ O Ca(C ₂ H ₃ O ₂) ₂	37.4	36.0	34.7	33.8	33.2		32.7		33.5		
Acetate .1H ₂ O Ca(C ₂ H ₃ O ₂) ₂										31.1	29.7
Chloride CaCl ₂ .6H ₂ O	59.5	65.0	74.5	102							
Chloride CaCl ₂ .2H ₂ O							136.8	141.7	147.0	152.7	159
Nitrate .4H ₂ O Ca(NO ₃) ₂	102.0	115.3	129.3	152.6	195.9						
Nitrate .3H ₂ O Ca(NO ₃) ₂					237.5	281.5					
Nitrate Ca(NO ₃) ₂									385.7		363.6
Sulfate .2H ₂ O CaSO ₄	0.176	0.193		0.209	0.210		0.205	0.197			0.162
Hydroxide Ca(OH) ₂	0.185	0.176	0.165	0.153	0.141	0.128	0.116	0.106	0.094	0.085	0.077

Table 3-3. Results of Lime Dissolution Rate Effected by Inorganic Additives

Additive Name	Additive % Weight in Solution	pH Stat Upper Limit	Average pH of Solution	Average Temp of Solution °C	Dissolution Rate of Lime $\times 10^8$ gmol/cm ² -sec.
Pure Water	0%	7.00	6.49	49.04	6.05
Tap Water	0%	7.00	6.95	51.05	6.39
NH ₄ Cl	2%	7.00	6.97	49.43	30.29
	10%	7.00	7.02	48.56	133.97
	20%	7.00	7.04	51.02	888.84
NH ₄ NO ₃	2%	7.00	6.94	46.81	20.41
	10%	7.00	6.98	50.81	117.26
NH ₄ I	2%	7.00	6.95	47.98	16.74
	10%	7.00	7.02	51.15	80.18
(NH ₄) ₂ SO ₄	2%	7.00	6.89	47.43	9.04
	10%	7.00	6.95	51.59	7.44
NH ₄ C ₂ H ₃ O ₂	2%	7.00	7.02	47.28	21.32
CaCl ₂	2%	7.00	6.22	53.91	7.56
	10%	7.00	6.38	53.49	9.19
NaCl	10%	7.00	5.20	53.44	6.79

Figure 3-1. Lime Dissolution Rate Under Different Additive Solutions as a Function of Additive Concentrations.

Figure 3-2. Lime Dissolution Rate Effected by Ammonium Compounds.

Figure 3-3. Lime Dissolution Rate versus Temperature as Derived From Activation Energy Formula.

Figure 3-4. Measured Solution pH versus Time for Lime Dissolution Without Additives.

Figure 3-5. Measured Solution pH versus Time for Lime Dissolution With 2% NH_4Cl .

CHAPTER 4: PILOT SCALE VERIFICATION OF THE EFFECT OF INORGANIC ADDITIVES ON THE DISSOLUTION RATE AND SO₂ UPTAKE EFFICIENCY

A pilot spray dryer experiment has been conducted to test the effect of NH₄Cl added to the Ca(OH)₂ slurry in the spray dryer. This test was designed to determine any change in SO₂ removal due to the change in lime dissolution as determined from previous laboratory experiments. The spray dryer inlet temperature was kept at about 300°F (150°C). The volumetric flow rate was about 150 cfm (4.2 m³/min.) with an average gas residence time in the dryer of approximately 11 seconds. The inlet SO₂ concentration was around 2500ppm. The concentration of CaO by weight was 10%. The approach to saturation temperature was controlled to about 30°F. The real time spray dryer outlet temperature and SO₂ removal across the spray dryer are shown in Figure 4-1 and Figure 4-2. Figure 4-1 shows the baseline test results while Figure 4-2 is the results for a test with 0.5% NH₄Cl by weight addition to the slurry. From the dissolution rate data in Chapter 3, this concentration should result in a dissolution rate approximately twice that of calcium hydroxide in regular water.

It can be seen that after the addition of NH₄Cl the SO₂ removal experienced a continuous increase. After about 15 minutes the removal reached a steady state with an average removal of more than 60%. This removal was about 50% above the baseline removal of about 40% at steady state. These results are shown in Figure 4-3, where the SO₂ removal efficiency is plotted versus the lime dissolution rate for these two experiments. These tests indicate that SO₂ uptake is very sensitive to dissolution rate, as would be expected, because the majority of the reaction occurs in the constant rate drying period where dissolution rate is a rate limiting step. Figure 4-3 indicates a linear relationship between removal and dissolution rate.

Figure 4-1. Real Time SO₂ Removal Efficiency Across Spray Dryer and Spray Dryer Outlet Temperature versus Time (Baseline).

Figure 4-2. Real Time SO₂ Removal Efficiency Across Spray Dryer and Approach to Saturation Temperature versus Time (With NH₄Cl).

Figure 4-3. Plot of SO₂ Removal versus Lime Dissolution Rate for Experimental Results from Pilot Plant Testing.

CHAPTER 5: THE EFFECT OF NH_4Cl ON LIMESTONE DISSOLUTION

Because the addition of NH_4Cl resulted in large increases in lime dissolution rates, and SO_2 removal in spray dryer tests, laboratory tests were also performed on limestone. The limestone randomly chosen for the tests was a natural lithographic limestone named F2-14 supplied by Dravo Lime company, Pittsburgh, Pennsylvania. This limestone could not be easily compressed into a disk as in the case of lime. The limestone was cut into disks for these tests. The test results are shown in Table 5-1, and the NH_4Cl effects on limestone dissolution rate at room temperature and pH upper limit 5.4 are shown in Figure 5-1. It can be seen that with an increase of NH_4Cl concentration, the dissolution rate of limestone increased steadily. Higher temperatures also enhanced the limestone dissolution rate. At higher pH values, the dissolution rate of limestone was depressed, but with NH_4Cl in solution, the dissolution rate at higher pH values can still be larger than the dissolution rate without NH_4Cl at lower pH values. This implies that current wet FGD systems could be operated at higher pH values with the addition of certain amounts of NH_4Cl . The benefit of operating at higher pH is to prevent or minimize corrosion.

Table 5-1. Comparison of Results for F2-14 Limestone Dissolution Rate in Different Conditions

NH ₄ Cl Conc. % by Weight	pH Upper Limit	Average pH	Average Temperature °C	Rate x10 ⁹ gmol/cm ² -s
0.0%	5.40	5.10	23.30	3.93
2.0%	5.40	5.10	25.44	9.55
10.0%	5.40	5.17	23.79	15.92
20.0%	5.40	5.18	21.85	16.96
0.0%	5.80	5.38	54.10	0.74
10.0%	5.80	5.85	52.28	28.36
10.0%	6.05	6.08	53.67	17.51

Figure 5-1. F2-14 Limestone Dissolution Rate versus Different NH_4Cl Concentration at Room Temperature and pH Upper Limit 5.40.

CHAPTER 6: SPRAY DRYER MODELING

Introduction to "SPRAYMOD-M"

The spray dryer mathematical model (SPRAYMOD) is intended to be used as a predictive model for spray dryer performance. This model was initially developed by Damle, S.A. (Damle, 1985) and later modified by Partridge, P.G. Jr. (Partridge, 1987), and recently converted to FORTRAN. A brief physical, chemical, and mathematical description forming the basis of the model are given in the following.

The initial version was observed to be less sensitive to the effects of slurry concentration and SO_2 concentration than the observed data (Partridge, 1987). SPRAYMOD tended to underpredict at low slurry concentrations and overpredict at high slurry concentrations. SPRAYMOD neglected the liquid phase mass transfer resistance and calculated the SO_2 removal during the evaporation/reaction process considering only the individual resistance that was dominate.

By considering the mass transfer approach in SPRAYMOD to be in error, the modified model borrowed the material and energy balance calculations from the original program. The modified model (SPRAYMOD-M) aimed at developing a comprehensive model for the constant rate period using a mechanistic approach which combines the individual resistances that affect the SO_2 absorption rate into a single relationship. Both the gas phase mass transfer and liquid phase mass transfer coefficients were included as well as a relationship to predict the resistance to lime dissolution. The model was based on film theory and treated the atomized slurry droplet

as a sphere with the fluid phase uniformly distributed around the discrete individual sorbent particles. This approach was said to allow predictions of the mass transfer coefficients and the enhancement due to increasing solid concentration as evaporation proceeds. Efficiency predictions using the modified model had been compared with the pilot-plant data taken from the pilot spray dryer/baghouse facility using a slipstream at the University of Tennessee's stoker fired boilers.

The development of a spray dryer mathematical model can be generalized by the following: Two processes simultaneously take place in the desulfurization of flue gas by spray dryers. One is the drying of the slurry droplets, and another is the SO_2 mass transfer and reaction within the sorbents contained in the slurry droplets.

Drying Processes Concerning the desulfurization in the spray dryer, the drying process can be roughly divided into two major periods. The first period is called the constant rate drying period. In this period, the solid particle concentration in the slurry droplet does not affect the water evaporation rate, and this period continues until the moisture of the droplets falls below the critical moisture content which is about 30% by weight of water in the droplets. The second period directly follows the first period, and is named the falling rate period. In this period, the solid particles contained in the droplets begin to touch each other, and the moisture has to diffuse through the solid matrix. This period continues until the moisture in the dried droplets achieve an equilibrium with the moisture in the surrounding gas, and this moisture content in the dried droplets is called the equilibrium moisture content which is around 5% by weight of water in the dried droplets.

The Constant Rate Period: The mathematical descriptions of the drying process also follows the

above discussion. In the constant rate drying period, the heat is transferred from the gas phase to the droplets, and water vapor is transferred from the droplet surface to the gas phase. The transfer coefficients can be determined by the following correlations (Ranz and Marshall, 1952).

$$Sh = 2 + \alpha Re^\beta Sc^\gamma \quad (2)$$

$$Nu = 2 + \alpha Re^\beta Pt^\gamma$$

where

$Sh = k_d d_d / D$ is Sherwood Number for mass transfer.

$Re = d_d v \rho / \mu$ is Reynolds Number based on droplet diameter.

$Sc = \mu / \rho D$ is Schmidt Number.

$Nu = h d_d / k$ is Nusselt Number for heat transfer.

$Pt = C_p \mu / k$ is Prandtl Number.

k_d is gas-phase mass transfer coefficient.

d_d is droplet diameter.

D is water vapor diffusivity in gas phase.

v is the relative velocity between gas and droplet.

ρ is gas density.

μ is gas kinetic viscosity.

h is gas phase heat transfer coefficient.

k is gas phase thermal conductivity.

C_p is gas specific heat.

α, β, γ are constants, 0.6, 0.5, and 0.33, respectively.

By assuming quiescent droplet-gas system, a rigorous analysis of the evaporation process gives the rates of mass and heat transfer (Bird et al, 1960):

$$N_w = 2\pi D c d_d \ln\left[\frac{1 - x_g}{1 - x_d}\right] \quad (3)$$

and

$$Q = 2\pi k d_d (T_g - T_d) \left[\frac{\varepsilon}{e^\varepsilon - 1} \right] \quad (4)$$

where ε is the dimensionless heat-transfer rate factor, and for water is given by:

$$\varepsilon = \frac{9}{\pi} \cdot \frac{N_w C_{p,l}}{k d_d} \quad (5)$$

and

N_w is the molar rate of water evaporation.

Q is the heat transfer rate.

c is the mean molar density of gas phase.

x_g is water vapor mole fraction in the bulk gas phase.

x_d is the equilibrium water vapor mole fraction at the droplet surface.

T_g is the temperature in bulk gas phase.

T_d is the temperature of the droplets.

$C_{p,l}$ is specific heat of water vapor.

The heat transferred from gas phase to the droplets is used to evaporate the moisture in the droplets, and the heat and mass transfer are related by:

$$Q = N_w \lambda + \frac{\pi d_d^3}{6} \rho_1 C_{p,l} \frac{dT_d}{dt} \quad (6)$$

where

ρ_1 is the density of the droplets.

λ is the latent heat of vaporization at T_d .

t is time.

The water vapor at the droplet surface is in equilibrium with the water in the droplet, therefore:

$$x_d = f(T_d) \quad (7)$$

x_d is given by the water vapor partial pressure at T_d .

Equations (3), (4), (6), and (7) are combined to solve for the drying process, but there are seven unknowns (N_w , x_d , x_g , Q , T_d , T_g , t) contained in these four equations. So additional relationships must be found in order to solve this problem. The additional equations are found from the gas and droplet mass and energy balances.

In the gas phase mass and energy balance, the gas temperature T_g , the gas phase water vapor mole fraction x_g , and SO_2 mole fraction, x_s are solved by the following equations.

$$C_s \frac{dT_g}{dt} = - Q \quad TN \quad (8)$$

$$\frac{1}{MW (1 - x_g)} \frac{d x_g}{dt} = N_w \quad TN \quad (9)$$

$$\frac{1}{MW (1 - x_g)} \frac{d x_s}{dt} = - N_s \quad TN \quad (10)$$

TN is the number of droplets per gram of dry inlet gas, which is known.

MW is the molecular weight of dry inlet gas.

N_s is the SO_2 molar transfer rate from gas phase to droplets.

C_s is the humid heat, and is given by

$$C_s = 0.24 + 0.446 \frac{18 x_g}{MW (1 - x_g)} \quad (11)$$

The above three equations introduce two additional unknowns which are x_s and N_s . N_s can be solved by considering the SO_2 removal processes.

The droplet energy balance is given by equation (4). In the droplet mass balance, the

weight of moisture in a droplet W , the weight of active sorbent (unreacted sorbent) in a droplet S , and the total weight of a droplet WD , are given by the following equations.

$$\frac{dW}{dt} = - 18 N_w \quad (12)$$

$$\frac{dS}{dt} = - MW_s \cdot N_s \quad (13)$$

$$\frac{d WD}{dt} = - 18 N_w + 64 N_s \quad (14)$$

where MW_s is the molecular weight of the active sorbent.

The above three equations introduce three new unknowns which are W , S , and WD . WD is directly related to W and S , however.

All the equations listed above should be adequate in solving the drying problem, except that N_s should be obtained by considering SO_2 mass transfer, or the absorption process.

The Falling Rate Period: When the moisture in the droplet reaches the critical moisture content at which the solid particles in the droplets begin to touch each other and form a continuous phase (Parti and Palancz, 1974), the solid concentration starts to influence the drying rate, and the falling rate period begins. The falling rate drying period continues until the moisture content in the droplets reaches the equilibrium moisture content. There is no simple correlations to describe this drying process. A linear drying rate between the critical moisture content and the equilibrium moisture content is assumed in the model.

$$\text{Drying Rate} = \left(\frac{\text{Drying Rate Based on Gas}}{\text{Phase Resistance Alone}} \right) \left(\frac{X - X_e}{X_c - X_e} \right)^n \quad (15)$$

where

X is moisture content at time t.

X_e is equilibrium moisture content.

X_c is critical moisture content.

n is a dimensionless parameter, for linear relation n=1.

SO₂ Absorption Process SO₂ removal in spray dryer absorbers is also modelled according to the drying periods (Partridge, 1987); the constant rate period and the falling rate period.

Constant Rate Period: The conceptual model which serves as the basis for model development of the constant rate period has the following characteristics:

1. Instantaneous reaction between SO₂ and Ca(OH)₂ occurs in ionic form in the liquid phase.
2. Droplets possess spherical symmetry.
3. Elementary Ca(OH)₂ particles in the atomized slurry droplets are stagnant due to the high apparent slurry viscosity.
4. CO₂ is taken as an inert gas.
5. Reactant sorbent Ca(OH)₂ first undergoes dissolution, followed by diffusion toward the reaction zone. The overall rate is controlled by the slowest of these steps.
6. The effect of product precipitation on sorbent dissolution can be approximated by considering the dissolution rate to be proportional to the lime fraction remaining in the solid phase.

A schematic diagram for the constant rate period model is given in Figure 6-1.

The SO₂ absorption process can be considered as four separate steps. SO₂ first diffuses from the bulk gas phase to the droplet surface, absorbs into the droplets and diffuses from the

droplet surface to the reaction zone. On the solid side, Ca(OH)_2 first dissolves from the solid phase into the liquid phase, then diffuses to the reaction zone where it reacts with SO_2 .

The rate of SO_2 mass transfer through the gas film can be given by:

$$N_s = k_g \pi d_d^2 c (x_g - x_d) \quad (16)$$

The rate of SO_2 mass transfer through the liquid film can be given by:

$$N_s = k_l \pi d_d^2 (C_{Ai} - 0) \frac{X_0}{X} \quad (17)$$

The sorbent (lime) dissolution rate is given by:

$$R_d = k_s \pi d_p^2 (C_s - C_B) N_p \quad (18)$$

The sorbent mass transfer rate in the liquid film is given by:

$$R_p = k_{Bl} \pi d_d^2 (C_B - 0) \frac{x_0}{x_0 - x} \quad (19)$$

where

k_g and k_l are mass transfer coefficients for SO_2 at gas side and liquid side respectively (cm/s).

R_d is the rate of lime dissolution.

k_s is the mass transfer coefficient for sorbent dissolution (cm/s).

k_{Bl} is the liquid side Ca(OH)_2 mass transfer rate (cm/s).

d_p is the sorbent solid particle diameter (cm).

N_p is the number of sorbent solid particles in a droplet.

N_s may then be obtained (by considering other relationships in addition to the above four) as:

$$N_s = \frac{\pi d_d^2 \left[\frac{C x_g}{H_A} + \frac{D_{Bl} C_S}{D_l} \right]}{\frac{1}{k_s H_A} + \frac{1}{k_l} + \frac{d_d^2 \delta R_L}{d_p^2 N_p D_l}} \quad (20)$$

where

D stands for the diffusivity, replacing k (the mass transfer coefficient).

H_A is the Henry's Law constant for SO_2 .

δ is the film thickness surrounding the sorbent solid particles d_p .

Some of the details are omitted in the above derivation of the model, and the reader is referred to the references for more description.

Falling Rate Period: Because reaction rates between the gas and the solid slow considerably in the falling rate period, this portion of the reaction period is not considered in detail. The falling rate period is modeled by using empirical relationships dependent on particle porosity and approach to saturation temperature, which is indicative of the residual moisture in the captured particles.

Derivation of Simplified Model for SO_2 Removal in Spray Dryer

In order to find a simple relationship for the spray drying desulfurization processes, a simplified equation which assumed gas phase mass transfer control has been derived. The SO_2 removal is explicitly related to the drying time of the droplet, and its calculated results are compared to experimental data and sophisticated model prediction.

If the gas phase SO_2 mass transfer resistance becomes the limiting step for the overall

process in the constant rate period, a simple correlation can be derived between the SO₂ removal efficiencies and the residence time of the liquid phase. Even though this hypothesis is very rough, the results of this derivation will give a clear picture of the relationships in the spray dryer desulfurization process.

As shown in Figure 6-2 which outlined the spray dryer chamber and the coordinate, the flue gas flow rate is Q (m³/Hr.), and the spray dryer inlet SO₂ concentration is C_0 . The Ca(OH)₂ slurry volumetric flow rate is N (m³/Hr.). The origin of x coordinate is right at the nozzle. At position x the concentration of SO₂ is C , and at position $x + dx$ the concentration of SO₂ becomes $C-dC$. Assume the SO₂ mass transfer coefficient in the air is k_g , the initial droplet diameter (at the birth of the droplet) averaged over the distribution is d_{d0} , and the droplet diameter averaged over the constant rate period (over time) is d_d .

When flue gas moves down from point x to point $x+dx$, the SO₂ concentration is reduced from C to $C-dC$. This concentration reduction is due to SO₂ overcoming the gas phase resistance and diffusing to the droplets. Therefore, this concentration reduction is equal to the mass transfer flux times the overall droplet surface area in the volume $S \cdot dx$, times the flue gas residence time in the volume $S \cdot dx$, and be divided by the volume $S \cdot dx$. Since N/Q is the slurry volume per volume of air, the number of droplets per volume of air is:

$$\frac{N}{Q \frac{1}{6} \pi d_{d0}^3} \quad (21)$$

$$\frac{N}{Q} \frac{1}{6} \pi d_{d0}^3 \pi d_d^2 (S \cdot dx) = \frac{6N d_d^2 S dx}{Q d_{d0}^3} \quad (22)$$

The overall droplet surface area in the volume $S \cdot dx$ is: The flux of SO_2 in terms of gas phase resistance is: $k_g C$, here the concentration of SO_2 at the droplet surface is assumed to be zero.

The residence time of flue gas in the volume $S \cdot dx$ is $dt = S \cdot dx / Q$. So

$$-dC = \frac{k_g C \cdot \frac{6N d_d^2 S dx}{Q d_{d0}^3} \cdot dt}{s dx} \quad (23)$$

and

$$\frac{dC}{C} = - \frac{6N d_d^2 k_g dt}{Q d_{d0}^3} \quad (24)$$

Integrate t from 0 to t and C from C_0 to C ,

$$\frac{C}{C_0} = e^{-\frac{6N d_d^2 k_g t}{Q d_{d0}^3}} \quad (25)$$

The removal efficiency is $\eta = 1 - C/C_0$, therefore:

$$\eta = 1 - e^{-\frac{6N d_d^2 k_g t}{Q d_{d0}^3}} \quad (26)$$

From equation 26, the understanding of the hygroscopic additive effects is straight

forward. Since the hygroscopic additives effect to retain moisture on the droplet surface, the constant period will be prolonged, and therefore t will be larger than that without additives in the slurry droplets. If t is increased, the η will be increased assuming other conditions to be the same. A illustration of the η versus t for the typical conditions in our mini-pilot spray dryer is shown in Figure 6-3 where the air flow rate used is 150 cfm, droplet diameter $d_d=d_{d0}=100$ micrometers, and $k_g=5.884 \times 10^{-5} T^{1.75}$ where $T=70^\circ\text{C}$. The typical slurry input in the spray dryer is about 4 gallon/hour if the approach to saturation temperature is kept around 20°F (11°C). The upper limit for the slurry input ia about 6gallon/hr. The slurry volumetric input depends on the approach to saturation temperatures if the slurry concentration is constant.

From Figure 6-3, we can also see that since under the typical baseline conditions the constant rate period last in about 1.4 seconds, the time 1.4 seconds is located at the middle of the curve with the steepest slope. This means that the slight increase of the constant rate period by hygroscopic additives can give rise to a dramatic increase of SO_2 removal efficiency.

Another phenomenon which was observed in the spray dryer can also be explained by Figure 6-3. As shown in Figure 6-3, the differences between the removal efficiencies of SO_2 with and without additives seem to be larger at higher approach to saturation temperatures, and smaller at lower approach to saturation temperatures. It can be reasonably deduced that higher approach to saturation temperatures relate to lower slurry volume inputs, while lower approach to saturation temperatures relate to higher slurry volume inputs. Since higher slurry volume inputs also result in the longer constant rate period, as shown in Figure 6-3, the longer constant rate period may well pass the most steep slope section of the curve, so the additives probably will not effect the SO_2 removal efficiencies very well in the lower approach to saturation temperatures.

The lower slurry volume inputs on the other hands result in shorter constant rate period, and the shorter constant rate period corresponds to the steep slope section of the curves in Figure 6-3, so the additives probably will effect the removal efficiencies more significantly at higher approach to saturation temperature.

Application of "SPRAYMOD-M" on Baseline Test Results

The baseline prediction of SO₂ removal was based on the available SPRAYMOD-M model from the University of Tennessee, and the results were compared to the baseline experimental data. As shown in Figure 6-4, in the model prediction of SO₂ removal efficiency versus Ca/S molar ratio the model results fit the SO₂ removal from our experiments, but underpredicted the SO₂ removal from the EPRI's High Sulfur Test Center. This is due to the fact that the Ca(OH)₂ particles in our slaked lime have larger particle sizes which were measured on a Coulter Counter. As shown in Figure 6-5, the mode of our particle size is about 6.08 micrometers while the mode of well slaked lime should be less than 4 micrometers.

Table 6-1 gives a list of the parameters and standard operating conditions which are typical in the mini-pilot plant. In the model, the stoichiometric Ca/S molar ratio was varied from 0 to 3.0 (in the experiment, the ratio was kept at about 1.5 which was used as the standard condition in the model), and the approach to saturation temperature from 5°C (9°F) to 30°C (54°F) (the approach to saturation temperature of 20°F, about 11°C, was used as the standard condition). When either of them was changed, the other was kept constant in the standard condition.

Figure 6-6 gives the comparison of the model predictions with experimental data on

baseline SO₂ removal versus approach to saturation temperature. It can be seen from Figure 6-6 that the model fits the data very well. The simplified model predictions are also shown in Figure 6-6. The simplified model used the same constant rate time as that of the "SPRAYMOD-M". It can be seen that the simplified model over-predicted the baseline SO₂ removal.

Modification of "SPRAYMOD-M" for Hygroscopic Additive Effects

The Mechanism of Hygroscopicity The hygroscopicity of the additives can be found from the following theory. Since feeds of insoluble solids from slurries and pastes (referred to as suspensions) have negligible vapor-pressure lowering effects, the total drying time of the lime slurry droplets containing insoluble and dissolved solids can be evaluated as the drying time of the liquid containing dissolved species. Since some salts (especially the sodium salts) have high solubilities (Table 6-2) and vapor-pressure lowering effects, the dissolved salts can increase the liquid phase residence time of the droplets. Since most of the reactions occur in the liquid phase, this prolonged residence time has a significant effect on SO₂ removal.

The relationship between saturation ratio and droplet (containing dissolved material) size is given by Hinds as the following:

$$x_d = \frac{p}{p_s} = \frac{1}{1 + \frac{6imM_w}{M_s \rho \pi d_p^3}} \cdot \exp\left(\frac{4\gamma M_w}{\rho R T d_p}\right) \quad (27)$$

where,

P is the partial pressure of water vapor at the droplet surface, any units.

P_s is the saturation pressure at the plane surface of pure water, same units as P.

M_s is the molecular weight of dissolved salt, g/mole.

m is the weight of dissolved salt in the droplet, g.

i is the number of ions each salt molecule forms when dissolves (2 for NaOH).

ρ is the density of the solvent (water), g/cm³.

M_w is the molecular weight of the solvent (water), g/mole.

γ is the surface tension of the solvent (water), dyn/cm.

d_p is the droplet diameter, cm.

R is the ideal gas law constant, dyn•cm/K.

T is the absolute temperature of the droplet, K.

In the spray dryer, the Kelvin effect may be small because of the relatively large droplet size (Kelvin effect is prominent when the droplet sizes are less than 0.1 μ m), but from the above formula we can see how the additive salts affect the partial water vapor pressure at the droplet surface. If other variables are held constant, the salts change the partial pressure through im/M_s , i.e. the mole of additive in a droplet times the ion number each molecule of the additive forms. From equation 27, higher value of the im/M_s term results in greater reduction of the droplet surface partial pressure. A comparison of the im/M_s term for different substances is shown in Table 6-3. As shown in Table 6-3, NaOH is the most hygroscopic additive in retaining the moisture.

From equation (27) we can see that x_d is directly related to the partial water vapor pressure on the droplet surface. The partial water vapor pressure is affected by the additive through im/M_s term which is the properties of additives. In order to reduce the water evaporation from the droplets, one possible way is to reduce the driving force for water vapor mass transfer from the droplet surface to the bulk gas phase (i.e. reduction of $x_d - x_g$). The hygroscopic additive effects is to reduce the water vapor pressure P on a droplet surface, thus reduce x_d , and $x_d - x_g$. The enhancement of sorbent utilization due to the hygroscopicity of additives can be explained as following. When water evaporates from the droplets in the spray dryer, the salt concentration in a droplet will increase with decreasing droplet size if the salt is highly soluble

because the mass of the salt remains constant and it is only the water that evaporates. Thus, a given mass of dissolved salt serves to reduce the vapor pressure at the droplet surface to a greater degree as droplet size decreases. The size change is reflected in the term πd_d^3 .

The water vapor pressure lowering effects by NaOH can be seen from Figure 6-7 where the water vapor pressure is above NaOH solution plane surface (Perry's Chemical Engineer's Handbook, 1984). As NaOH concentration is increased, the partial water vapor pressure is greatly reduced.

Figure 6-8 gives the pressure ratio versus the droplet size under the influence of additives. The pressure ratio is the ratio of the water vapor pressure on the droplet surface to the water vapor pressure on a plane surface of pure water. The calculation was made from equation (27). The saturated concentration of $\text{Ca}(\text{OH})_2$ is 1280 mg/l which is at the temperature of 50°C.

Combined with the equation for the calculation of water vapor pressure on the droplet surface in the original model, equation (27) was used to modify the water vapor pressure on droplet surface to predict the hygroscopic additive effects. The original model was basically unchanged in terms of the basic principles for drying and SO_2 removal. When an input data file is going to be made, a question will be shown on the screen to ask if the additive is added into the sorbent slurry. If the answer is 'NO', the input data file will be the baseline input data file. If the answer is 'YES', a series of consecutive questions will be followed to ask the properties of the additive used, and thus create an additive input data file. Changes have been made in the main program to accommodate all the input data file. The output file will indicate if additive is used, and if used, in what quantities.

With the addition of NaOH 500 mg/liter into the 10% $\text{Ca}(\text{OH})_2$ slurry, Figure 6-9 shows

the model prediction of SO₂ removal versus approach to saturation temperature. As can be seen from the Figure 6-9, if the approach to saturation temperature is below 30°F, the model slightly under-predicted the removal. If the approach to saturation temperature is above 30°F, the model under-predicted the SO₂ more with the increase of approach to saturation temperature.

The model predictions on the effects of other two additives (NaCl and NaHCO₃) are shown in Figure 6-10. The model over-predicted the removal if the approach to saturation temperature is below 28°F, but under-predicted the removal if the approach to saturation temperature is above 28°F. There are no significant differences between the two additives in terms of SO₂ removed based on the model prediction.

The Mechanisms of Dissolution Rate Enhancing Additives

The ammonium chloride has been tested on spray dryer for its effects on desulfurization. The test results showed that with 0.5% weight addition of NH₄Cl, the net SO₂ removal increase can be as much as 20%. The film thickness in SPRAYMOD-M has been adjusted to reflect the dissolution rate increase. The baseline continuous experimental monitoring of SO₂ removal and spray dryer outlet temperature is shown in Figure 6-11, and with 0.5% NH₄Cl in the slurry is shown in Figure 6-12. In both Figures, the dashed lines stand for the modified SPRAYMOD-M predictions. The Fortran model is listed in Appendix where the modified hygroscopic additive subroutine and dissolution rate enhancing additive subroutine are included.

Table 6-1. SPRAYMOD-M Operating Parameters and Standard Conditions

List of Parameters	SI Units	Eng. Units
Inlet Gas Conditions		
Inlet Gas Temperature	149°C	300°F
% Water in Inlet Gas	1%	1%
Inlet SO ₂ Concentration	2500 ppm	2500 ppm
Molecular Weight of Dry Inlet Gas	28.9	28.9
Operating Parameters		
Approach to Saturation Temperature	11°C	20°F
Stoichiometric Ca/S Molar Ratio	1.5	1.5
Mass Fraction of Sorbent in Fresh Solids	1.0	1.0
Recycle Solids Ratio by Mass	0.0	0.0
Mass Fraction of Sorbent in Recycle	0.0	0.0
Residence Time of Gas Phase	10 sec.	10 sec.
Flow System in Spray Dryer	Plug	Plug
Sorbent Properties		
Inlet Droplet Diameter	100 um	100 um
Inlet Droplet Temperature	15.6°C	60°F
Form of Sorbent	Slurry	Slurry
Sorbent Particle Diameter	6.08 um	6.08 um
Molecular Weight of Sorbent	74	74
Density of Solid Sorbent	2.24 g/cm ³	140 lb/ft ³
Critical Moisture Content	29.2%	29.2%
Equilibrium Moisture Content	6%	6%
Dry Sorbent Reaction Rate Coefficient	0.0	0.0
Assumed Spray Dryer Efficiency	50%	50%
Program Parameters		
Maximum Allowable Time Step	0.1 sec	0.1 sec
Time Between Printouts	0.5 sec	0.5 sec
Time Step Control Parameter	0.01 sec	0.01 sec

Table 6-2. Solubilities of Ca^{2+} and Na^+ Substances (g in 100g H_2O) [Perry, 1984].

Substances	Temperature				
	20°C	30°C	40°C	60°C	80°C
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	74.5	102	-	-	-
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	-	-	-	136.8	147.0
$\text{Ca}(\text{OH})_2$	0.165	0.153	0.141	0.116	0.094
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-	0.2090	0.2097	0.2047	-
NaHCO_3	9.6	11.1	12.7	16.4	-
NaCl	36.0	36.3	36.6	37.3	38.4
$\text{NaOH} \cdot \text{H}_2\text{O}$	109	119	129	174	-
Na_2SO_4	-	-	48.8	45.3	43.7

Table 6-3. Comparison of the im/M_s term for different substances.

Substance	NaOH	NaHCO_3	NaCl	CaCl_2	Na_2SO_4
i	2	3	2	3	3
M_s	40	84	58.5	111	142
im/M_s	0.05m	0.036m	0.034m	0.027m	0.021m

Figure 6-1. Schematic Diagram for SO_2 Absorption into Slurry Droplets.

The symbols in Figure 6-1 stand for:

- x_g is the mole fraction of SO_2 in the bulk gas phase.
- x_d is the mole fraction of SO_2 at the droplet surface (gas-liquid interface).
- C_{Ai} is the concentration of SO_2 at the interface (in gmole/cm^3).
- C_B is the concentration of Ca(OH)_2 in the bulk liquid phase (gmole/cm^3).
- C_S is the saturation concentration of Ca(OH)_2 at the liquid phase (gmole/cm^3).
- x is the distance from the gas-liquid interface to the reaction zone (cm).
- x_0 is the liquid film thickness (cm).

Flue Gas Volumetric Flow Rate = Q
 Slurry Volumetric Flow Rate = N

Figure 6-2. Schematic Drawing for Derivation of Spray Dryer Desulfurization Model.

Figure 6-3. SO₂ Removal versus Ca/S Molar Ratio for Baseline Ca(OH)₂

Figure 6-4. Baseline SO₂ Removal versus Approach to Saturation Temperature.

Figure 6-5. Ca(OH)_2 Particle Size Distribution Measured by Coulter Counter.

Figure 6-6. Baseline SO₂ Removal versus Approach to Saturation Temperature.

Figure 6-7. Water Vapor Partial Pressure Over NaOH Solution Plane Surface.

Figure 6-8. Ratio of Pressure of Droplet Surface to Plane Pure Water Surface versus Droplet Size

Figure 6-9. Comparison of Model Prediction and Experimental Data on SO₂ Removal versus Approach to Saturation Temperature.

Figure 6-10. Comparison of Model Prediction and Experimental Data on SO₂ Removal versus Approach to Saturation Temperature.

Figure 6-11. SO₂ Removal and Spray Dryer Outlet Temperature Continuous Monitoring as Compared to Model Prediction (Baseline).

Figure 6-12. SO₂ Removal and Approach to Saturation Temperature Continuous Monitoring and Model Prediction (0.5% NH₄Cl).

CHAPTER 7: CONCLUSIONS

This study has focused on studying the effect of various predetermined additives on lime dissolution rate in solution. This is deemed important because of the importance of dissolution in the uptake of SO_2 in spray dryers.

Six organic additives were tested for their effect on lime dissolution rate. These were phenol, sucrose, glycerin, ammonium acetate, urea, and ethyl-alcohol. For the three additives phenol, sucrose, and glycerin in the additive concentration range of less than 10% by weight, phenol has the greatest effect on lime dissolution rate. When phenol concentrations reach 20%, the lime dissolution rate declines because not all the phenol in water is dissolved. Sugar enhances the dissolution rate of lime steadily. Adding glycerin to the solution seems to result in little improvement on lime dissolution over pure water, and an increase in glycerin concentration leads to no further improvement in the lime dissolution rate. For all the organic additives, ammonium acetate has the greatest effect in enhancing lime dissolution rate. Urea increases lime dissolution slightly. Alcohol decreased the lime dissolution rate.

Six inorganic additives were also tested for their effects on lime dissolution rate. They were NH_4Cl , NH_4NO_3 , NH_4I , $(\text{NH}_4)_2\text{SO}_4$, CaCl_2 , and NaCl . It was found that most ammonium inorganic compounds have the ability to increase lime dissolution rate. This phenomenon was first considered a chemical reaction, but the activation energy calculated from further tests on NH_4Cl dissolution rate versus temperature indicated that NH_4Cl accelerated the mass transfer process. With a 2% NH_4Cl weight concentration, the lime dissolution rate increased by almost 40 times. The experiment results also showed that ammonium sulfate does not give similar results on lime dissolution enhancement. Further studies found that the insignificant effect by

ammonium sulfate is due to the lower solubility of calcium sulfate which could deposited back onto the calcium hydroxide and prevent further dissolution into the solution.

The results of the bench scale and pilot scale tests on additives have been incorporated into a numerical predictive model called SPRAYMOD-M. This model is a comprehensive coupled heat and mass transfer description of the reaction mechanisms responsible for removal of SO₂ in spray dryers. The model has been modified to incorporate the results from these studies concerning the improvements in removal efficiency and dissolution rate via the use of additives. These effects include increased hygroscopicity and enhanced dissolution of the parent calcium hydroxide particles into the slurry water.

The revised model has been shown to give reasonable agreement with experimental data for changes in SO₂ removal efficiency. These changes are from the addition of additives that either enhance the dissolution rate of the lime in solution, or increase the hygroscopicity of the solids, thereby decreasing the evaporation rate.

REFERENCES

Shelly, D.P. and Gupta, P.N., "Slaking System Design for Reactive Limes at Four Corners," In Proceedings of Effective Use of Lime for Flue Gas Desulfurization, The National Lime Association, D.H. Stowe, ed., Denver Colorado, September 27-28, 1983.

Keener, T.C., Wang, J. and Khang, S.J., "Final Report: The Effect of Additives on Lime Dissolution Rates," Project OCRC/4-10, The Ohio Coal Development Office, Columbus, Ohio, July, 1995.

Bird, R.B., W.E. Stewart, and E.N. Lightfoot, "Transport Phenomena," John Wiley and Sons, New York, (1960).

Damle, A.S., "Modelling of SO₂ Removal in Spray Dryer Flue Gas Desulfurization System", EPA-600/7-85-038, December, (1985).

Hinds, W.C., "Aerosol Technology", John Wiley & Sons, Inc., (1982).

Parti, M. and B. Palancz, "Mathematical Model for Spray Drying," Chem. Eng. Sci., Vol. 29, pp.355-362, (1974).

Partridge, G.P. Jr., "A Mechanistic Spary Dryer Mathematical Model Based on Film Theory to Predict Sulfur Dioxide Absorption and Reaction by A Calcium Hydroxide Slurry in the Constant Rate Period", Ph.D. Dissertation, The University of Tennessee, Knoxville, December, (1987).

Perry, R.H. and D. Green, "Perry's Chemical Engineer's Handbook", 6th Edition, McGraw-Hill, Inc., (1984).

Ranz, W.E. and W.R. Marshall, Jr., "Evaporation From Droplets," Chem. Eng. Prog., Vol. 48, No. 3, pp.141-46, 173-80, (1952).

APPENDIX

Appendix A: Additive Effects Applied to "SPRAYMOD-M" PROGRAM SD

*

*

**

*

*

REAL WI, SI, MG, AT, SR, MF, RR, MR, RT, D0, TW,
&DP, MS, SG, XC, RK, MT, P1, TE, WO, XU, ES, XF, W0,
&TN, NP, LX, WW, CM, CI, EF, CS
INTEGER OP, CON, N
CHARACTER Q

*

** Set Default values

*

N=0
CON = 0
WI= 5.6
SI= 1012.
MG= 29.4
TI= 172.
TE= 300.
AT= 19.4
SR= 1.
MF= 1.
RR= 0.
MR= .3
RT= 17.5
OP= 2
D0= 77.
TW= 37.8
DP= 3.25
MS= 74.1
SG= 2.24
XC= 29.2
XE= 6.
RK= 0.
P1= 60.
EF = 60.
MT= 0.1

*

** INLET GAS CONDITIONS

*

```
10 N=N+1
  IF (N .LT. 2) THEN
    CALL IGC(TI, WI, MG, SI)
    RTI=TI
    RWI=WI
    RMG=MG
    RSI=SI
  ENDIF
  IF (N .GT. 1) THEN
    PRINT*, 'CHANGE INLET GAS CONDITIONS?'
    READ*, Q
    IF (Q .EQ. 'Y' .OR. Q .EQ. 'y') THEN
      CALL IGC(TI, WI, MG, SI)
      RTI=TI
      RWI=WI
      RMG=MG
      RSI=SI
    ELSE
      TI=RTI
      WI=RWI
      MG=RMG
      SI=RSI
    ENDIF
  ENDIF
```

*

** OPERATING PARAMETERS

*

```
  IF (N .LT. 2) THEN
    CALL OPAR(AT, SR, MF, RR, MR, RT, OP)
    RAT=AT
    RSR=SR
    RMF=MF
    RRR=RR
    RMR=MR
    RRT=RT
    ROP=OP
  ENDIF
  IF (N .GT. 1) THEN
    PRINT*, 'CHANGE OPERATING PARAMS?'
    READ*, Q
    IF (Q .EQ. 'Y' .OR. Q .EQ. 'y') THEN
```

```

    CALL OPAR(AT, SR, MF, RR, MR, RT, OP)
    RAT=AT
    RSR=SR
    RMF=MF
    RRR=RR
    RMR=MR
    RRT=RT
    ROP=OP
ELSE
    AT=RAT
    SR=RSR
    MF=RMF
    RR=RRR
    MR=RMR
    RT=RRT
    OP=ROP
ENDIF
ENDIF
*
** INPUT SORBENT PROPS
*
IF (N .LT. 2) THEN
    CALL SPROP(D0, TW, DP, MS, SG, XC, XE, RK)
    RD0=D0
    RTW=TW
    RDP=DP
    RMS=MS
    RSG=SG
    RXC=XC
    RXE=XE
    RRK=RK
ENDIF
IF (N .GT. 1) THEN
    PRINT*, 'CHANGE SORBENT PROPS?'
    READ*, Q
    IF (Q .EQ. 'Y' .OR. Q .EQ. 'y') THEN
        CALL SPROP(D0, TW, DP, MS, SG, XC, XE, RK)
        RD0=D0
        RTW=TW
        RDP=DP
        RMS=MS
        RSG=SG
        RXC=XC

```

```

RXE=XE
RRK=RK
ELSE
D0=RD0
TW=RTW
DP=RDP
MS=RMS
SG=RSG
XC=RXC
XE=RXE
RK=RRK
ENDIF
ENDIF

```

*

** INPUT ADDITIVE PARAMETERS

*

```

CHARACTER ADDITIVE, HYGADD, DISSADD
REAL DISSRT, CONCADD
PRINT*, 'Do you have additive in your slurry?'
READ*, ADDITIVE
IF (ADDITIVE .EQ. 'y' .OR. ADDITIVE .EQ. 'Y') THEN
  PRINT*, 'Is the additive hygroscopic?'
  READ*, HYGADD
  IF (HYGADD .EQ. 'y' .OR. HYGADD .EQ. 'Y') THEN
    CALL HYGPARA(ADDFORM, NOIONS, ADDWEIGHT, MSADD, PARA)
  ELSE
    PARA=1.0
    PRINT*, 'Is the additive dissolution rate enhancing?'
    READ*, DISSADD
    IF(DISSADD .EQ. 'y' .OR. DISSADD .EQ. 'Y') THEN
      PRINT 1001, DISSRT
1001  FORMAT(1X, 'Enter the dissolution rate of lime under additive, gmole/cm2-s
      $      (, E5.2 ,)')
      READ*, DISSRT
      PRINT 1002, CONCADD
1002  FORMAT(1X, 'Enter the concentration of the additive in g/liter slurry (, F5.2
      $      ,)')
      READ*, CONCADD
      CALL DISSPARA (DISSRT, KS, FILMT)
    ELSE
      PARA=1.0
      DISSRT= 6.05E-8
    
```

```

        CONCADD=0.0
        PRINT*, 'Sorry, we haven't find a way to mathematically fit this additive into
$         the model'
        ENDIF
    ENDIF
ENDIF

```

```

*
** PROGRAM PARAMETERS
*

```

```

    IF (N .LT. 2) THEN
        CALL PRPAR(MT, P1)
        RMT=MT
        RP1=P1
    ENDIF
    IF (N .GT. 1) THEN
        PRINT*, 'CHANGE PROGRAM PARAMETERS?'
        READ*, Q
        IF (Q .EQ. 'Y' .OR. Q .EQ. 'y') THEN
            CALL PRPAR(MT, P1)
            RMT=MT
            RP1=P1
        ELSE
            MT=RMT
            P1=RP1
        ENDIF
    ENDIF
ENDIF

```

```

*
** SEND DATA TO OUTPUT FILE
*
    CHARACTER *12 OUT
    PRINT*, ''
    PRINT*, ''
    PRINT*, 'ENTER NAME OF OUTPUT FILE '
    READ*, OUT
    OPEN(UNIT=3, FILE=OUT, ACCESS='DIRECT',
    & FORM='FORMATTED', STATUS='NEW', RECL=200)
    WRITE(UNIT=3, FMT=101) TI, WI, MG, SI, AT, SR,
    & MF, RR, MR, RT, OP, D0, TW, DP, MS, SG, XC, XE,
    & RK
101 FORMAT('TI=', F5.1, 'WI=', F5.1, 'MG=', F5.1,
    & 'SI= ', F8.1, 'AT=', F5.1, 'SR=', F5.1, 'MF=',
    & F5.1, 'RR=', F5.1, 'MR=', F5.1, 'RT=', F5.1,

```

```

& 'OP=', I3, 'D0=', F5.1, 'TW=', F5.1, 'DP=',
& F5.1, 'MS=', F5.1, 'SG=', F5.1, 'XC=', F5.1, 'XE=',
& 'RK=', F5.1)
*
** CONVERSIONS
*
  TI=TI+273
  WI=WI*0.01
  SI=SI*.000001
  LX=(MF+RR*MR)/(1+RR)
  D0=D0*.0001
  TW=TW+273.15
  DP=DP*.0001
  XC=XC*.01
  XE=XE*.01
*
** CALC ADIABATIC SAT TEMP
*
  CALL AST(WI, MG, TI, TE, AT, CS)
*
** OVERALL MAT'L & ENERGY BALANCE
*
  CALL OMEB(TE, AT, TI, XE, WI, SI, SR, MS, RR,
& MF, MG, MR, D0, SG, DP, WO, XU, ES, XF, W0,
& TN, NP)
*
** INITIALIZE DROPLET AND GAS PHASE VARIABLES
*
  WWW=XF*W0
  CM=W0*(1-XF)*LX/MS
  CI=W0*(1-XF)*(1-LX)/MS
*
** BEGIN EFFICIENCY CALCS FOR PLUG OR BACKMIX FLOW
*
  IF (OP .EQ. 1) THEN
    CALL PLUG(TI, WI, SI, TW, D0, W0, WWW, XF,
& XE, CM, CI, SG, EF, UT, MT, DP, NP, MS, CON,
& CS, TN, MG, XU, XC, RT, ES, T, RK)
    IF (CON .EQ. 1) GO TO 100
  ELSE
    CALL MIXED(WI, SI, TW, D0, W0, WWW, XF,
& XE, CM, CI, SG, P1, EF, UT, MT, DP, NP, MS, CON,
& XU, XC, RT, ES, T, RK, WO, TE)

```

```

ENDIF
IF (CON .EQ. 1) GO TO 100
WRITE(UNIT=3, FMT=201) EF
201 FORMAT('EF= ', F5.3)
CLOSE(UNIT=3, STATUS='KEEP')
PRINT*, 'ANOTHER RUN?'
READ*, Q
IF (Q .EQ. 'Y' .OR. Q .EQ. 'y') THEN
    GO TO 10
ENDIF
*****
100 END
*****
**
**
**
    SUBROUTINE IGC(TI, WI, MG, SI)
    REAL TI, WI, MG, SI
    PRINT 101, TI
101 FORMAT(1X, 'ENTER INLET GAS TEMP, C (' F5.1, ')')
    READ*, TI
    PRINT 201, WI
201 FORMAT(1X, 'ENTER INLET % WATER VAPOR, (' F5.1, ')')
    READ*, WI
    PRINT 301, MG
301 FORMAT(1X, 'ENTER MW OF DRY GAS, (' F5.1, ')')
    READ*, MG
    PRINT 401, SI
401 FORMAT(1X, 'ENTER INLET SO2 CONC, ppm (' F8.1, ')')
    READ*, SI
    RETURN
    END
*
*
    SUBROUTINE OPAR(AT, SR, MF, RR, MR, RT, OP)
    REAL AT, SR, MF, RR, MR, RT
    INTEGER OP
    PRINT 101, AT
101 FORMAT(1X, 'ENTER APPR. TO SAT. TEMP, C (' F5.1, ')')
    READ*, AT
    PRINT 201, SR
201 FORMAT(1X, 'ENTER STOICHIOMETRIC RATIO, (' F5.1, ')')
    READ*, SR

```

```

PRINT 301, MF
301 FORMAT(1X, 'ENTER FRACTION OF REAGENT IN FRESH SOLIDS, (' F5.1, ')
&')
READ*, MF
PRINT 401, RR
401 FORMAT(1X, 'ENTER RECYCLE SOLIDS MASS RATIO (' F5.1, ')')
READ*, RR
PRINT 501, MR
501 FORMAT(1X, 'ENTER MASS FR. REAGENT IN RECYCLE, (' F5.1, ')')
READ*, MR
PRINT 601, RT
601 FORMAT(1X, 'ENTER GAS RESIDENCE TIME, SEC (' F5.1, ')')
READ*, RT
PRINT 701, OP
701 FORMAT(1X, 'ENTER 1 FOR PLUG FLOW, 2 FOR MIXED, (' I3, ')')
READ*, OP
RETURN
END
*
*
SUBROUTINE SPROP(D0, TW, DP, MS, SG, XC, XE, RK)
REAL D0, TW, DP, MS, SG, XC, XE, RK
PRINT 101, D0
101 FORMAT(1X, 'ENTER INLET DROPLET DIAM, um (' F5.1, ')')
READ*, D0
PRINT 201, TW
201 FORMAT(1X, 'ENTER DROPLET TEMP, C (' F5.1, ')')
READ*, TW
PRINT 301, DP
301 FORMAT(1X, 'ENTER SORBENT PARTICLE DIAM, um (' F5.1, ')')
READ*, DP
PRINT 401, MS
401 FORMAT(1X, 'ENTER MW OF SORBENT, (' F5.1, ')')
READ*, MS
PRINT 501, SG
501 FORMAT(1X, 'ENTER SPECIFIC GRAVITY OF SORBENT, (' F5.1, ')')
READ*, SG
PRINT 601, XC
601 FORMAT(1X, 'ENTER CRITICAL MOISTURE CONTENT, % (' F5.1, ')')
READ*, XC
PRINT 701, XE
701 FORMAT(1X, 'ENTER EQUILIBRIUM MOISTURE CONTENT, % (' F5.1, ')')
READ*, XE

```

```

PRINT 801, RK
801 FORMAT(1X, 'ENTER DRY SORBENT RXN RATE, CC/MOL-S (', F5.1, ')')
READ*, RK
RETURN
END

```

*

*

```

SUBROUTINE PRPAR(MT, P1)
REAL MT, P1
PRINT 101, MT
101 FORMAT(1X, 'ENTER MAX INTEGRATION TIME STEP, S (', F5.1, ')')
READ*, MT
PRINT 201, P1
201 FORMAT(1X, 'ENTER ASSUMED EFFICIENCY OF SYSTEM, % (', F5.1, ')')
READ*, P1
RETURN
END

```

*

*

```

SUBROUTINE AST(WI, MG, TI, TE, AT, CS)
REAL WI, MG, TI, TE, AT, WP, HI, T1, T2, T3, E1, E2, E3,
&TS, YP, PS, L, CS
INTEGER J
WP=WI*760
HI=WP*18/MG/(760-WP)
CS=.24+.45*HI
T1=330.
L=597.64-0.275*(T1+TI-546.3)
PS=EXP(20.426-5138.8/T1)
YP=PS*18/MG/(760-PS)
E1=TI-T1-(YP-HI)*L/CS
J=1
IF (ABS(E1) .LT. 0.1) GO TO 20
J=2
T2=T1+1.
L=597.64-0.275*(T2+TI-546.3)
PS=EXP(20.426-5138.8/T2)
YP=PS*18/MG/(760-PS)
E2=TI-T2-(YP-HI)*L/CS
IF (ABS(E2) .LT. 0.1) GO TO 20
J=3
10 T3=T1-E1*(T1-T2)/(E1-E2)
L=597.64-0.275*(T3+TI-546.3)

```



```

PS=EXP(20.426-5138.8/T3)
YP=PS*18/MG/(760-PS)
E3=TI-T3-(YP-HI)*L/CS
IF (ABS(E3) .LT. 0.1) GO TO 20
IF (ABS(E1) .LT. ABS(E2)) THEN
  T2=T1
  E2=E1
ENDIF
E1=E3
T1=T3
GO TO 10
20 CONTINUE
IF (J .EQ. 1) TS=T1
IF (J .EQ. 2) TS=T2
IF (J .EQ. 3) TS=T3
TE=AT+TS
PRINT*, 'SAT TEMP = ', TS
RETURN
END

```

*

*

```

SUBROUTINE OMEB(TE, AT, TI, XE, WI, SI, SR, MS, RR,
&MF, MG, MR, D0, SG, DP, WO, XU, ES, XF, W0, TN, NP)
REAL TE, AT, TI, XE, WI, SI, SR, MS, RR, MF, MG, MR,
&D0, SG, DP, PS, HS, TM, L, CS, HO, WO, RH, XU, HI,
&GW, GS, ES, XF, W0, TN, NP
PS=EXP(20.426-5138.8/(TE-AT))
HS=PS*18./MG/(760-PS)
TM=(TI+TE)/2
L=597.64-0.55*(TM-273.15)
CS=0.24+0.45*HS
HO=HS-AT*CS/L
WO=HO/(HO+18/MG)
PS=EXP(20.426-5138.8/TE)
RH=WO*760/PS
XU=RH*XE
HI=WI*760*18/MG/760/(1-WI)
GW=1.01*(HO-HI)
GS=SI*SR*MS*(1.+RR)/MF/MG/(1.-WI)
ES=SR*(1+RR*MR/MF)
XF=GW/(GW+GS)
W0=0.52356*D0**3*SG/(1+(SG-1)*XF)
TN=GW/XF/W0

```

```

NP=((D0/DP)**3)*(1-XF)/(1+(SG-1)*XF)
RETURN
END

```

*

*

```

SUBROUTINE PLUG(TI, WI, SI, TW, D0, W0, WW, XF,
&XE, CM, CI, SG, EF, UT, MT, DP, NP, MS, CON,
&CS, TN, MG, XU, XC, RT, ES, T, RK)
REAL TI, WI, SI, TW, D0, WD, WW, XF,
&XE, CM, CI, SG, EF, UT, MT, TG, XW, XS,
&TD, T, ST, D, W, X, W0,
&TM, DS, DW, CT, CO, PW, XD, WM, FW, VS, LP,
&CL, F, FS, DP, CS, TN, DG, SD, MG, DX
INTEGER I
I=0
TG=TI
XW=WI
XS=SI
TD=TW
T=0.
ST=0.
D=D0
WD=W0
W=WW
X=XF
UT=0.

```

*

** DROPLET & GAS MAT'L ENERGY BAL.

*

```

40 TM = (TD+TG)/2
I=I+1
DS = 2.951E-5*TM**1.5
DW = 5.062E-5*TM**1.5
CT = 0.012194/TM
CO = 1.82E-7*TM+.0000079
PW = EXP(20.426-5138.8/TD)
XD = PW/760.
IF (XD .GE. 1.) XD = 0.9999
IF (X .LT. XE) XD=XD*X/XE

```

*

** RATE OF WATER EVAP

*

```

IF (X .GE. XU) THEN

```

```

WM = 6.2832*DW*CT*D*ALOG10((1.-XW)/(1.-XD))
IF (X .LT. XC) WM = WM*(X-XU)/(XC-XU)
ELSE
  WM = 0.
  FW=0.
ENDIF
RL=(CM-ABS(ST))/CM
* SO2 ABS RATE FOR DRY STAGE
IF (X .LT. 0.01) THEN
  IF (RL .LT. .001) THEN
    SM=0.
  ELSE
    SM=-RK*XS*CT*RL*CM
  ENDIF
  FW=WM*18
  FS=SM*64
  GO TO 60
ENDIF
REAL XL
XL = XU*6.1
IF (X .LT. XL) THEN
  IF (RL .LT. .001) THEN
    SM=0
  ELSE
    SM=-RK*XS*CT*RL*CM
  ENDIF
  FW=WM*18
  FS=SM*64
  GO TO 60
ENDIF
*
** SO2 ABS RATE FOR WET SORBENT
*
FW=WM*18.
IF (RL .LT. 0.001) THEN
  F = 0.
  SM = 0.
  FS = 0.
  GO TO 60
ENDIF
VS = (1-X)/(1+(SG-1)*X)
LP = DP
LP = (RL*(LP**3))**0.3333

```

```

    CL = 0.00188-1.174E-5*(TD-273.15)
* FILM THICKNESS
    REAL BT, FILMT, FILMTL
    BT=(1/VS**0.3333)-1
    FILMT=0.5*BT*LP
    FILMTL=0.5*LP
* RATE REDUCTION DUE TO BLINDING
    RF = 1+(2.108*ABS(ST)+CI)/(CM-ABS(ST))
* CALC DIFFUSIVITY, MTC'S
    REAL TCD, PN, DAL, DBL, KG, KAL, KALL
    TCD = TD-273.15
    PN = (1.3272*(20-TCD)-.001053*(TCD-20)**2)/(TCD+105)
    DAL = (5.1735E-8*TD)/(1.002*10**PN)
    DBL = (5.472E-8*TD)/(1.002*10**PN)
    KG = 2*DS/D
    KAL = DAL/FILMT
    KALL = 13.1595*DAL/D
    IF (KAL .LT. KALL) KAL = KALL
    IF (FILMT .GT. FILMTL) FILMT = FILMTL
* CALC DENSITY & HENRY'S CONST.
    REAL RHO, KO, HA
    IF (TCD .LT. 45) RHO = 1.006615-.0003616*TCD
    IF (TCD .LT. 65) RHO = 1.012141-.000483*TCD
    IF (TCD .GE. 65) RHO = 1.020478-.0006102*TCD
    IF (TCD .LT. 45) KO = .13846*TCD-.55
    IF (TCD .LT. 65) KO = .18376*TCD-2.6176
    IF (TCD .GE. 65) KO = .2281143*TCD-5.492191
    KO = KO*10**4
    HA = ((2.88745E-4)*(KO-760))/(RHO*TD)
* COMBINED RATE
    REAL R, C, NP, MS
    R=1/(KG*HA)+1/KAL+(FILMT*RF*D**2)/(NP*DAL*LP**2)
    C=(CT*XS)/(HA)+(DBL*CL)/(DAL*MS)
    F = -((3.1421593*D**2)*C)/R
    SM=F
    FS=F*64.06
* CHECK FILM DISSOLUTION
*   REAL COND
*   INTEGER CON
*   COND=(3*(LP**2)*NP*(DAL**2))/(2*FILMT*(D**3)*(KAL**2))
*   IF (COND .GT. 1) THEN
*       PRINT*, 'DISSOLUTION IN FILM IMPORTANT'
*       PRINT*, ' '

```

```

*      PRINT*, 'MODEL DOES NOT APPLY'
*      CON = 1
*      GO TO 100
*      ENDIF
* CONTROLLING RATE DETERMINATION
  REAL GRATE, DRATE, MODELR, CONCB
  GRATE=KG*3.141593*(D**2)*CT*XS
  DRATE=3.141593*(LP**2)*NP*DBL/(FILMT*RF)*CL/MS
  CONCB=CL/MS+F*FILMT*RF/(3.141593*(LP**2)*NP*DBL)
  MODELR=-F
  IF (GRATE .LT. MODELR) THEN
    F = -GRATE
    SM=F
    FS=F*64.06
    GO TO 60
  ENDIF
  IF (CONCB .LT. 0) THEN
    F = -DRATE
    SM=F
    FS=F*64.06
  ENDIF
* HEAT TRANSFER RATE
  60 IF (WM .EQ. 0 .AND. ABS(TD-TG) .LT. 0.2) THEN
    Q=0.
  ELSE
    REAL EP
    EP = 1.289*WM/CO/D
    IF (EP .LT. .00001) EP=.00001
    Q=6.2832*CO*D*(TG-TD)*EP/(EXP(EP)-1)
  ENDIF
* DERIVATIVE FUNCTIONS
  F1=(Q-WM*10080)/WD
  F2=-FW-FS
* INTEGRATION TIME STEP
  REAL DT, D1, D2
  IF (F1 .EQ. 0) THEN
    D1 = 1000
  ELSE
    D1 = .01*(TD-273)/ABS(F1)
  ENDIF
  IF (F2 .EQ. 0) THEN
    D2 = 1000
  ELSE

```

```

      D2=.01*WD/ABS(F2)
    ENDIF
    DT=D1
    IF (D2 .LT. D1) DT=D2
    IF (DT .GT. MT) DT=MT
  * CHANGE IN GAS PHASE VARIABLES
    CS=.24+(.446*18*XW)/(MG*(1-XW))
    DG=Q*DT*TN/CS
    TG=TG-DG
    SD=SM*DT*TN*(1-XW)*MG
    XS=XS+SD
    DX=WM*DT*TN*(1-XW)*MG
    XW=XW+DX
    XS=XS/(1+DX)
    XW=XW/(1+DX)
  * CHANGE IN DROPLET VARIABLES
    T=T+DT
    ST=ST+SM*DT
    UT=-ST/CM
    TD=TD+F1*DT
    WD=WD+F2*DT
    W=W-FW*DT+18*SM*DT
    IF (W .LT. 0.) W=0.
    X=W/WD
    D=((WD+(SG-1)*W)/SG/.52356)**(.33333)
  * CHECK FOR ZERO REMOVAL
    IF (SM .EQ. 0) GO TO 50
  * CHECK TIME
    IF (T .GE. RT) GO TO 50
    IF (T .LT. RT) GO TO 40
  * REMOVAL EFFICIENCY
    50 EF=ES*UT
    PRINT*, 'EFFICIENCY = ', EF
    PRINT*, 'TIME = ', T
  100 RETURN
  END
*
*
  SUBROUTINE MIXED(WI, SI, TW, D0, W0, WWW, XF,
    &XE, CM, CI, SG, P1, EF, UT, MT, DP, NP, MS, CON,
    &XU, XC, RT, ES, T, RK, WO, TE)
  REAL P2, WI, SI, TW, D0, W0, WWW, XF,
    &XE, CM, CI, SG, P1, EF, UT, MT, DP, NP, MS,

```

```

&XU, XC, RT, ES, T, RK, WO, TE, TG,
&XW, TD, ST, WD, W, X, LP
INTEGER CON, I, J, N
P2=0.
IF (ES .LT. 1) P2=ES
P1=P1/100
J=0
I=0
30 I=I+1
IF (I .LT. 2) THEN
    P1=P1*100
    P1=P1/100
ENDIF
XS=SI*(1-P1)*(1-WO)/(1-WI)
TG=TE
XW=WO
TD=TW
T=0.
ST=0.
D=D0
WD=W0
W=WW
X=XF
UT=0.
N=0
*
** DROPLET & GAS MAT'L ENERGY BAL.
*
40 TM = (TD+TG)/2
N=N+1
DS = 2.951E-5*TM**1.5
DW = 5.062E-5*TM**1.5
CT = 0.012194/TM
CO = 1.82E-7*TM+.0000079
PW = EXP(20.426-5138.8/TD)
XD = PW/760.
IF (XD .GE. 1.) XD = 0.9999
IF (X .LT. XE) XD=XD*X/XE
*
** RATE OF WATER EVAP
*
IF (X .GE. XU) THEN
    WM = 6.2832*DW*CT*D*ALOG10((1.-XW)/(1.-XD))

```

```

    IF (X .LT. XC) WM = WM*(X-XU)/(XC-XU)
ELSE
    WM = 0.
    FW=0.
ENDIF
    RL=(CM-ABS(ST))/CM
* SO2 ABS RATE FOR DRY STAGE
    IF (X .LT. 0.01) THEN
        IF (RL .LT. .001) THEN
            SM=0.
        ELSE
            SM=-RK*XS*CI*RL*CM
        ENDIF
        FW=WM*18
        FS=SM*64
        GO TO 60
    ENDIF
    REAL XL
    XL = XU*6.1
    IF (X .LT. XL) THEN
        IF (RL .LT. .001) THEN
            SM=0
        ELSE
            SM=-RK*XS*CI*RL*CM
        ENDIF
        FW=WM*18
        FS=SM*64
        GO TO 60
    ENDIF
*
** SO2 ABS RATE FOR WET SORBENT
*
    FW=WM*18.
    IF (RL .LT. 0.001) THEN
        F = 0.
        SM = 0.
        FS = 0.
        GO TO 60
    ENDIF
    VS = (1-X)/(1+(SG-1)*X)
    LP = DP
    LP = (RL*(LP**3))**0.3333
    CL = 0.00188-1.174E-5*(TD-273.15)

```



```

* FILM THICKNESS
  REAL BT, FILMT, FILMTL
  BT=(1/VS**0.3333)-1.
  FILMT=0.5*BT*LP
  FILMTL=0.5*LP

* RATE REDUCTION DUE TO BLINDING
  RF = 1+(2.108*ABS(ST)+CI)/(CM-ABS(ST))

* CALC DIFFUSIVITY, MTC'S
  REAL TCD, PN, DAL, DBL, KG, KAL, KALL
  TCD = TD-273.15
  PN = (1.3272*(20-TCD)-.001053*(TCD-20)**2)/(TCD+105)
  DAL = (5.1735E-8*TD)/(1.002*10**PN)
  DBL = (5.472E-8*TD)/(1.002*10**PN)
  KG = 2*DS/D
  KAL = DAL/FILMT
  KALL = 13.1595*DAL/D
  IF (KAL .LT. KALL) KAL = KALL
  IF (FILMT .GT. FILMTL) FILMT = FILMTL

* CALC DENSITY & HENRY'S CONST.
  REAL RHO, KO, HA
  IF (TCD .LT. 45) RHO = 1.006615-.0003616*TCD
  IF (TCD .LT. 65) RHO = 1.012141-.000483*TCD
  IF (TCD .GE. 65) RHO = 1.020478-.0006102*TCD
  IF (TCD .LT. 45) KO = .13846*TCD-.55
  IF (TCD .LT. 65) KO = .18376*TCD-2.6176
  IF (TCD .GE. 65) KO = .2281143*TCD-5.492191
  KO = KO*10**4
  HA = ((2.88745E-4)*(KO-760))/(RHO*TD)

* COMBINED RATE
  REAL R, C
  R=1/(KG*HA)+1/KAL+(FILMT*RF*D**2)/(NP*DAL*LP**2)
  C=(CT*XS)/(HA)+(DBL*CL)/(DAL*MS)
  F = -((3.1421593*D**2)*C)/R
  SM=F
  FS=F*64.06

* CHECK FILM DISSOLUTION
  REAL COND
  COND=(3*(LP**2)*NP*(DAL**2))/(2*FILMT*(D**3)*(KAL**2))
  IF (COND .GT. 1) THEN
    PRINT*, 'DISSOLUTION IN FILM IMPORTANT'
    PRINT*, ' '
    PRINT*, 'MODEL DOES NOT APPLY'
    CON = 1
  
```

```

        GO TO 100
    ENDIF
* CONTROLLING RATE DETERMINATION
    REAL GRATE, DRATE, MODELR, CONCB
    GRATE=KG*3.141593*(D**2)*CT*XS
    DRATE=3.141593*(LP**2)*NP*DBL/(FILMT*RF)*CL/MS
    CONCB=CL/MS+F*FILMT*RF/(3.141593*(LP**2)*NP*DBL)
    MODELR=-F
    IF (GRATE .LT. MODELR) THEN
        F = -GRATE
        SM=F
        FS=F*64.06
        GO TO 60
    ENDIF
    IF (CONCB .LT. 0) THEN
        F = -DRATE
        SM=F
        FS=F*64.06
    ENDIF
* HEAT TRANSFER RATE
    60 IF (WM .EQ. 0 .AND. ABS(TD-TG) .LT. 0.2) THEN
        Q=0.
    ELSE
        REAL EP
        EP = 1.289*WM/CO/D
        IF (EP .LT. .00001) EP=.00001
        Q=6.2832*CO*D*(TG-TD)*EP/(EXP(EP)-1)
    ENDIF
* DERIVATIVE FUNCTIONS
    F1=(Q-WM*10080)/WD
    F2=-FW-FS
* INTEGRATION TIME STEP
    REAL DT, D1, D2
    IF (F1 .EQ. 0) THEN
        D1 = 1000
    ELSE
        D1 = .01*(TD-273)/ABS(F1)
    ENDIF
    IF (F2 .EQ. 0) THEN
        D2 = 1000
    ELSE
        D2=.01*WD/ABS(F2)
    ENDIF

```

```

DT=D1
IF (D2 .LT. D1) DT=D2
IF (DT .GT. MT) DT=MT
* CHANGE IN DROPLET VARIABLES
T=T+DT
ST=ST+SM*DT
UT=-ST/CM
TD=TD+F1*DT
WD=WD+F2*DT
W=W-FW*DT+18*SM*DT
IF (W .LT. 0.) W=0.
X=W/WD
D=((WD+(SG-1)*W)/SG/.52356)**(.33333)
* CHECK FOR ZERO REMOVAL
IF (SM .EQ. 0) GO TO 50
* CHECK TIME
IF (T .GE. RT) GO TO 50
IF (T .LT. RT) GO TO 40
* REMOVAL EFFICIENCY
50 EF=ES*UT
P2=EF
IF (P2 .GT. 1) P2=1.
P3=ABS(P2-P1)
IF (P3 .GT. 0.02) THEN
  IF (I .EQ. 1) THEN
    PA=P1
    PB=(P1+P2)/2
    P1=(P1+P2)/2
    GO TO 30
  ENDIF
  PC=(P1+P2)/2
  IF (ABS(PC-PB) .LT. ABS(PB-PA)) THEN
    PA=PB
    PB=PC
    P1=(P1+P2)/2
    GO TO 30
  ENDIF
  IF ((PB-PC)/(PB-PA) .GT. 0) PC=(PA+PB)/2
  IF ((PB-PC)/(PB-PA) .LT. 0) PC=1.5*PB-PA/2
  P2=2*PC-P1
  PA=PB
  PB=PC
  P1=(P1+P2)/2

```

```

      GO TO 30
    ENDIF
    EF=(P1+P2)/2
    XS=SI*(1-EF)*(1-WO)/(1-WI)
    J=J+1
    IF (J .LT. 2) THEN
      IF (T .EQ. 0) GO TO 40
      IF (SM .EQ. 0) GO TO 50
      IF (T .GE. RT) GO TO 50
      GO TO 40
    ENDIF
    PRINT*, 'EFFICIENCY = ', EF
    PRINT*, 'TIME = ', T
100 RETURN
  END

```

```

SUBROUTINE HYGPARA (ADDFORM, NOIONS, ADDWEIGHT, MSADD, PARA)
REAL NOIONS, ADDWEIGHT, MSADD, PARA, MW, RHO
CHARACTER *(*) ADDFORM
PARAMETER RHO=1.0, MW=18.0
PRINT*, 'Enter the chemical formula of the additive added'
READ*, ADDFORM
PRINT 101, NOIONS
101 FORMAT(1X, 'Enter No. of ions one additive molecule generate when dissolute in
$      water, (', F3.1, ')')
READ*, NOIONS
PRINT 201, ADDWEIGHT
201 FORMAT(1X, 'Enter weight of additive added in one liter of slurry, g/liter (', F5.1,
$      ')')
READ*, ADDWEIGHT
PRINT 301, MSADD
301 FORMAT(1X, 'Enter the molecular weight of the additive, g/mole (', F5.1, ')')
READ*, MSADD
PARA=1.0/(1.0+(NOIONS*ADDWEIGHT*0.001*MW)/(MSADD*RHO))
RETURN
END

```

```

SUBROUTINE DISSPARA(DISSRT, KS, FILMT)
REAL DISSRT, KS, FILMT, FILMTL, COEFF, DELTCSAT
PARAMETER FILMTL=5.0E-5, COEFF=0.03
DELTCSAT=1.73E-5*0.03
KS=DISSRT/DELTCSAT

```

```
FILMT=1.98E-5/KS  
IF(FILMT<FILMTL) FILMT=FILMTL  
RETURN  
END
```

Appendix B: List of the Meaning of Code Variables in SPRAYMOD-M.

AT	Approach to saturation temperature (°C).
BT	A factor which uses water fraction relating droplet diameter to film thickness.
C	Overall SO ₂ removal rate numerator.
CI	Unreactive sorbent in a droplet as converted to Ca(OH) ₂ molar amount.
CL	Equilibrium solubility of Ca(OH) ₂ in water (g/cm ³) at temperature TD (°K).
CM	Initial molar amount of active sorbent in a droplet (mole).
CO	Thermal conductivity of air (cal/cm-sec.-°C).
CON	An integer constant.
COND.	Condition number to check if film dissolution is negligible.
CS	Humid heat of air at TI (cal./g dry air).
CT	Molar density of gas phase (gmole/cm ³).
D	Renewed droplet diameter after a period of time (cm).
D0	Inlet droplet diameter (um).
DAL	SO ₂ diffusivity in water (cm ² /s).
DBL	Ca(OH) ₂ diffusivity in water (cm ² /s).
DG	Total amount of heat transfer during DT.
DP	Sorbent particle diameter (um).
DRATE	Ca(OH) ₂ dissolution rate.
DS	Diffusivity of SO ₂ in air (cm ² /s).
DT	Time interval used for increment of time in spray drying process (sec.).
DW	Diffusivity of water vapor in air (cm ² /s).
DX	Total evaporated water during time DT.
EF	Total SO ₂ removal efficiency after time T.
ES	Stoichiometric molar ratio when there is recycled solids.
F	Overall SO ₂ removal rate.
F1	Droplet temperature change with time.
F2	Water vapor flux plus SO ₂ flux.
FILMT	Film thickness (cm).
FILMTL	Film thickness upper limit (cm).
FS	=F*64.06
FS	SO ₂ Flux (g/s).
FW	Water flux (g/s).
GRATE	Gas phase SO ₂ mass transfer rate.
GS	Amount of solids added in the slurry (g solids/g dry inlet air).
GW	Amount of water added in the spray chamber (g water in slurry/g dry inlet air).
HA	Henry's Law constant.
HI	The amount of water in the flue gas (g water/g dry air).

HO	The gas phase humidity in the spray dryer outlet.
HS	The amount of water in saturated gas at T1 (g water/g dry air).
KAL	SO ₂ liquid phase mass transfer coefficient (cm/s).
KALL	Lower limit of KAL.
KG	SO ₂ gas phase mass transfer coefficient (cm/s).
KO	Variable used for Henry's law constant calculation.
L	Latent heat of water vaporization at (T1+TI)/2 (cal/g).
LP	Renewed Ca(OH) ₂ particle diameter after a period of time.
L	Mass fraction of total reagent including recycled solids.
MF	Mass fraction of sorbent in fresh solids.
MG	Molecular weight of dry inlet gas (g/mole).
Modelr	= -F
MR	Mass fraction of sorbent in recycle.
MS	Molecular weight of sorbent (g/mole).
MT	Maximum allowable time step (sec. 0.1).
NP	Number of primary particles in a droplet.
OP	Flow system in spray dryer (OP=1 plug flow; OP=2 backmix).
OS	Form of sorbent (OS=1 slurry).
PI	Assumed spray dryer efficiency (%).
PN	Power coefficient for calculations of diffusivity in liquid.
PS	Water vapor saturation pressure at T1 (mmHg).
PW	Water vapor pressure at TD (mmHg).
Q	Rate of heat transfer to one droplet.
R	Overall SO ₂ removal rate denominator.
RH	Fractional relative humidity of outlet flue gas.
RHO	Density of water (g/cm ³).
RK	Dry sorbent reaction rate coefficient.
RL	Remaining fraction of active sorbent with respect to initial active sorbent.
RR	Recycle solids ratio by mass.
RT	Residence time of gas phase (sec.).
SD	Total amount of SO ₂ during DT.
SG	Density of solid sorbent (g/cm ³).
SI	Inlet SO ₂ concentration (ppm).
SM	=F
SM	Sorbent and SO ₂ reaction rate (gmole/s).
SR	Stoichiometric molar ratio.
ST	Utilization of sorbent.
T1	Assumed droplet temperature 57 (°C).
TCD	Droplet temperature (°C).
TD	Droplet temperature (°C).
TG	Renewed gas phase temperature after a period of time (K).
TI	Inlet gas temperature (°C).
TM	Average temperature of inlet and outlet of spray dryer (°C).

TN	Number of droplets atomized per g of dry inlet air.
TW	Inlet droplet temperature (°C).
UT	Total sorbent utilized after a period of time.
W	Renewed water weight in a droplet (g).
W0	Initial weight of a droplet (g).
WD	Renewed droplet weight after a period of time.
WI	% water in inlet gas (%).
WM	Water evaporation rate (gmole/s).
WO	% water in outlet gas (%).
WP	Partial water vapor pressure in inlet gas.
WW	Water weight in a droplet (g).
X	=W/WD Renewed mass fraction of water in slurry droplet.
XC	Critical moisture content (%).
XD	Fractional partial water vapor pressure at TD.
XE	Equilibrium moisture content (%).
XF	Mass fraction of water in feed slurry.
XS	Renewed gas phase SO ₂ concentration after a period of time (ppm).
XU	=RH*XE
XW	Renewed % water content in gas phase after a period of time.
YP	g water/g of dry air for saturated water at T1.