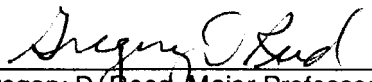
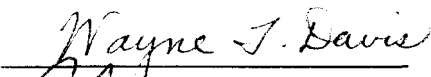
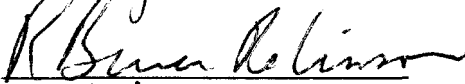


To the Graduate Council :

I am submitting herewith a dissertation written by Sambamurty Raju Dantuluri entitled "Limitation Of Sulfur Dioxide Removal In A FGD Spray Dryer Using Once Through Slaked Lime." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Civil Engineering.


Gregory D. Reed, Major Professor

We have read this dissertation
and recommend its acceptance :


Accepted for the Council :


Vice Provost
and Dean of The Graduate School

LIMITATION OF SULFUR DIOXIDE REMOVAL
IN A FGD SPRAY DRYER USING ONCE
THROUGH SLAKED LIME

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Sambamurty Raju Dantuluri

December 1988

To my wife Krishna
and
kids Ravi and Surendra

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ABSTRACT

The present study discusses the importance of slaking operation and its effect on the removal efficiency in a spray dryer operated FGD system using slaked lime slurry. Laboratory scale slaking experiments were run to look into various characteristics of resulting slurry. Pilot plant tests were made to quantify the effects of different parameters on spray removal efficiency. A vertical tower mill was used to grind calcium hydroxide slurry to attain smaller particle size. X-ray diffraction and SEM techniques were used to visualize the crystallinity and surface aspects of calcium hydroxide slurry. Sorbent particle size and surface area measurements were made for different slurries and an attempt was made to relate these parameters with the sorbent's performance in removing SO₂ across the spray dryer. A previous version of a mechanistic model for predicting SO₂ removal efficiency during constant rate period was modified to incorporate measured surface area of the sorbent into the model. The findings of the present work indicate that removal efficiencies increase with decrease in sorbent particle size. Removal efficiency is observed to increase with specific surface area of the sorbent, but there seems to be a limitation on the maximum possible efficiency that can be achieved. By increasing the surface area beyond certain values, the spray dryer system can be operated under gas-phase controlled conditions, which should give maximum possible efficiency. The new version of the model SPRAYMOD-N was used to mimic these conditions to arrive at the gas phase controlled efficiency and corresponding particle size to achieve those conditions. It is found that slaked lime slurry particles around 2.3 microns size can give an efficiency of around 75 percent in the spray dryer for an inlet SO₂ concentration of 1000 ppm, operated at a stoichiometric ratio (SR) of one and saturation approach temperature of 20⁰ F. Pilot tests conducted in this study with 2.4 micron Ca(OH)₂ slurry achieved this efficiency. The new version of the model for the constant rate period, was observed to

predict reasonably well for both the present pilot test data and previous sets of data collected over a period of time. Predicted efficiency values (with constant rate period only) fell off at higher SR values, showing the significance of the falling rate period at those conditions. The surface area incorporation into the model resulted in decreasing the gap between actual values and under predicted values from a previous version of the model.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION	1
II. LITERATURE REVIEW	6
A. Lime Slaking	6
B. Spray Absorption Process For SO ₂ Removal	12
C. Modeling of SO ₂ Removal in Spray Dryer	20
III. EXPERIMENTAL PROCEDURES	31
IV. RESULTS AND DISCUSSION	39
A. Studies With Modified Limes	39
B. Effect of Particle Size /Surface Area	48
C. Incorporation of Surface Area into Model	62
D. Comparison of SPRAYMOD-N with Pilot Plant Data	75
V. CONCLUSIONS	101
VI. RECOMMENDATIONS FOR FUTURE STUDY	104
LIST OF REFERENCES	105
APPENDIX : COMPUTER PROGRAM FOR SPRAYMOD-N	111
VITA	120

LIST OF TABLES

TABLE		PAGE
4-1	Experimental values for different Ca(OH)_2 slurries slaked in laboratory during the present study	42
4-2	Comparison of experimental values for crystallinity indices and surface areas for different slaked limes	47
4-3	Average pilot plant data for different slaked lime slurries . . .	50
4-4	Average particle diameters and corresponding surface area and efficiency values at $\text{SR}=1$	60
4-5	Comparison between calculated and measured values for the slaked lime specific surface areas.	67
4-6	Summary of model simulation conditions for different pilot plant data sets	89
4-7	Summary of important parameters of pilot plant data sets and figures showing the comparison between predictions and actual data	90

LIST OF FIGURES

FIGURE		PAGE
2-1	Damle model for wet particle stage	26
2-2	Partridge model for constant rate period	29
3-1	Schematic diagram of pilot plant	32
3-2	Sample curve for particle size measurement.	37
4-1	SEM micrograph for $\text{Ca}(\text{OH})_2$ from hot lime slaked in laboratory, 5000 X, magnification	43
4-2	SEM micrograph for $\text{Ca}(\text{OH})_2$ from regular lime slaked in laboratory, 5000 X, magnification	44
4-3	Spray dryer removal efficiency vs. stoichiometric ratio for 2.4 micron slaked lime	51
4-4	Spray dryer removal efficiency vs. stoichiometric ratio for 2.7 micron slaked lime	52
4-5	Spray dryer removal efficiency vs. stoichiometric ratio for $\text{Ca}(\text{OH})_2$ with 3.4 micron particles	53
4-6	Spray dryer removal efficiency vs. stoichiometric ratio for the three slaked limes	54
4-7	Particle size vs. removal efficiency at $\text{SR}=1$	56
4-8	Inverse of particle diameter vs. removal efficiency.	57
4-9	Specific surface area measured for different particle sizes ...	58
4-10	Specific surface area vs. removal efficiency.	61
4-11	Surface area vs. negative log penetration	63
4-12	SEM micrograph for 2.4 micron slaked lime slurry	64
4-13	Comparison of pilot plant data with SPRAYMOD-M predictions	66
4-14	Typical input parameters for SPRAYMOD-N	71
4-15	Comparison of predictions from SPRAYMOD-N and SPRAYMOD-M versions.	76

FIGURE		PAGE
4-16	Comparison of pilot plant data with SPRAYMOD-N predictions for 2.4 micron slaked lime.	78
4-17	Comparison of pilot plant data with SPRAYMOD-N predictions for 2.7 micron slaked lime.	79
4-18	Comparison of pilot plant data with SPRAYMOD-N predictions for regular slaked lime.	80
4-19	Residuals of prediction vs. pilot plant efficiency data	81
4-20	Linear Regression I, for specific surface area and inverse of particle diameter	84
4-21	Linear Regression II, for specific surface area and inverse of particle diameter	85
4-22	SPRAYMOD-N prediction for optimum particle size.	86
4-23	Comparison of SPRAYMOD-N predictions with actual pilot plant data for data sets 2 and 3.	91
4-24	Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 4.	92
4-25	Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 5	93
4-26	Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 6.	94
4-27	Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 7.	95
4-28	Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 8	96
4-29	Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 9	97
4-30	Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 10	98
4-31	Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 11 and 12	99

CHAPTER I

INTRODUCTION

A major portion of the electric utility power in the United States is generated through coal combustion in utility boilers (1). Sulfur dioxide emitted from these boilers has been identified as the major contributor to the environmental problems caused by acid deposition, frequently referred to as acid rain. It is estimated that approximately 25 million tons of sulfur dioxide is emitted into the atmosphere every year, from the stacks of the utility boilers (2). In order to curb these emissions, the Environmental Protection Agency (EPA) promulgated new emission standards in the early 1970's. With this, electric utilities have been faced with increasingly stringent air quality emission requirements for both new and existing fossil fuel-fired power plants. In order to meet the requirements, a number of effective and economic sulfur removal techniques have been under investigation in the last decade. General options studied by researchers for emission reduction strategies are (3)

1. Fuel changes - e.g., coal cleaning
2. Combustion process changes - e.g., fluidized bed combustion
3. Flue gas cleanup - e.g., wet and dry scrubbing
4. Operational changes - e.g., emission trading

All these options have their own advantages and disadvantages, however the utilities industry has recognized Flue Gas Desulfurization (FGD), a post-combustion removal of sulfur from stack gases, as a reliable and environmentally acceptable process.

Capital costs for FGD equipment have been about equal to those of the entire boiler for a new unit (4). As such the process selection is generally made after a rigorous study. More popular FGD technology is based upon a wet chemical process using lime (CaO) or

limestone (CaCO_3) as a reagent. This technique accounts for more than 80 percent of the systems now in use (5). However, in recent years one dry scrubbing method, spray drying, has emerged as the preferred option for many new coal-fired power plants that use low sulfur coals (5). In the spray drying process, calcium hydroxide (Ca(OH)_2) slurry or sodium carbonate solution (Na_2CO_3) is sprayed through an atomizer into a drying vessel. The goal of atomization is to produce droplets with a mean size of 50-75 microns in diameter (12). Hot flue gas containing sulfur dioxide enters either at the top or bottom of the vessel and is evenly distributed. The flue gas provides the heat necessary for drying of atomized absorbent droplets. While the spray droplets evaporate, they absorb and react with sulfur dioxide. A dry powder product is formed within a short time and falls to the bottom of the spray dryer. The flue gas exits the dryer to a particulate collection device, usually a fabric filter or an electrostatic precipitator, wherein the product and any fly ash are collected (7).

Spray dryer absorption systems have several advantages in comparison with conventional wet scrubbing systems. These include lower capital costs, decreased corrosion and scaling, and elimination of wet sludge. The principal drawback is inadequate SO_2 removal rates and high stoichiometric ratios of lime to SO_2 when this technology is applied to high sulfur eastern coals (8). Even though spray dryer technology has not yet been applied on a commercial basis for new power plants burning high sulfur eastern coals, it has been considered as a potential alternative to wet scrubbing in various studies. In a recent evaluation of various FGD technologies it has been indicated that improvements in lime stoichiometry and upgrades of electrostatic precipitators for high dust loadings will make spray dryer technology extremely competitive for retrofit application in the eastern United States (2).

Previous studies (9,10) looked into the effect of different variables on the removal efficiency of SO_2 in a spray dryer and bag house combination. Major variables that have been studied are lime stoichiometry, approach to saturation, recycled solids, flue gas residence

time in the spray dryer, atomizer speed and inlet flue gas temperature. However, efforts were not made to relate the efficiency of removal with the sorbent preparation, properties, and parameters involved in the slaking process. A recent pilot plant study (12) reports a lime utilization of only 50 percent when tested against an inlet SO₂ concentration of 2000 ppm, using a conventionally slaked lime. To improve the utilization, a number of new avenues need to be explored.

Norman (11) in a recent study, showed that higher removal efficiencies can be achieved by using non-air quenched lime. Higher removals were linked to the higher surface areas of the calcium hydroxide slurries, obtained from quick limes processed in a different manner. Regular slake lime with about one micron size particles was projected to achieve near stoichiometric lime utilization for a flue gas with 1000 ppm inlet SO₂ concentration.

Computer models can be of great help for predicting removal efficiencies in FGD operations. The use of computer models would either eliminate or minimize the laborious pilot plant study in assessing the effect of various operating parameters. Damle (6) developed a rigorous mathematical model based on simultaneous heat and mass transfer occurring in a droplet of Ca(OH)₂ in spray dryer. Even though this model has good predicting capabilities, it has some draw backs in the approach used for developing rate equations. Partridge et al. (13) modified the model to improve the ability of the basic model to predict the performance of a spray dryer, while maintaining a mechanistic approach. In the modified version rate equations are based upon a calculated value for sorbent surface area. Further improvements to the model were made in the present work by inputting a measured value for surface area and altering the rate equations accordingly. Pilot plant data from the present study were compared with predictions from the modified version of the model by inputting measured values for particle diameter and surface area. The new model was used to predict the limiting condition for maximum efficiency during the constant rate period, in a spray dryer operation. Various

other pilot plant data from different test programs over a period of time were also compared with the predictions from the new version of the model.

The objective of this work was to examine the validity of the extrapolation of previous research data, which indicated that a progressive decrease in sorbent particle size (or increase in surface area) would produce a proportional increase in SO₂ removal efficiency across a spray dryer. Laboratory/pilot plant data and computer models were used to facilitate this examination.

In this study, it is recognized that slaking aspects are important for achieving higher lime utilizations. Various parameters of slaking and their effect on the removal efficiency have been looked into. The relation between sorbent particle size and its effect in removing SO₂ have been studied. The particle size obtained during regular slaking may have some limitation on the removal efficiency. In order to visualize this aspect, smaller sorbent particle size has been obtained by grinding operation. The advantage of achieving smaller particles has been looked into.

The present study focuses on the approaches used in the previous work (11) to obtain improved removal efficiencies for high inlet SO₂ concentrations. Laboratory slaking tests were performed initially using different quicklimes to study the characteristics involved. Various slaked limes (obtained from quicklimes processed differently) and regular slaked lime (from conventional quicklime) with different particle sizes were tested in a pilot plant and sorbent characteristics were related to removal efficiencies. The size of the sorbent particle was reduced by using a vertical tower mill. A decrease in particle size resulted an improvement in SO₂ removal efficiency across the spray dryer. Sorbent surface area was measured by using a modified technique and linked to sorbent's reactivity with SO₂. Surface characteristics of the slaked lime were studied using Scanning Electron Microscopy. X-ray diffraction studies were made to determine the crystallinity indices of different slaked limes. This study also tries

to find out any limitations involved for the removal enhancement in a spray dryer using once through slaked lime.

CHAPTER II

REVIEW OF LITERATURE

A. LIME SLAKING:

Even though slaking aspects of the absorbent preparation are very important for an efficient spray drying operation, they are not documented in the literature to a large extent. The quality of raw materials is important to obtain a reagent of required properties. For lime, limestone is the major source of raw material. Limestone is a naturally occurring mineral with CaCO_3 as the major constituent. For FGD applications limestone with the highest CaCO_3 content possible is desirable, most having at least 90 percent CaCO_3 . Quicklime (CaO) is produced from limestone through a calcination step wherein calcium carbonate dissociates to calcium oxide and CO_2 . The calcination is carried out in either horizontal rotary or vertical kilns. In the United States, rotary kilns are most widely used (14). Calcined product is quenched with air, pulverized and transported to storage. Proper calcination conditions are important to produce lime of good quality. Reactivity of lime is a function of specific surface area and pore space which are related to temperature or time of calcination or both (15). In general soft burned limes are more reactive (14,16). The calcination process seems to be simple, however, there are many unsolved problems, both physical and chemical, relating especially to the accurate prediction of practical behavior of the resulting products. A new X-ray approach used by Clark et al. (17) aims to identify the problems. The powder diffraction method used by them showed clear structural differences between soft and hard burned high calcium limes. Eades and Sandberg (15) analyzed the calcination process by studying the products at different stages and at different conditions. They used Scanning Electron Microscope (SEM) techniques to visualize the surface of these products. It was concluded

that the nature of limestone or form of CaCO_3 crystal seems to influence the structure, surface area and porosity of the resulting oxide. The activity of the lime is a function not of any abnormal lattice but of its very minute crystal size and surface area. McClellan and Eades (18) successfully utilized the SEM technique to measure surface area of limes, which compare very well with porosimeter measurements. SEM methods are also used to study the development and distribution of pore space in calcium oxide obtained through calcination (19). These studies indicate the importance of calcination conditions and parent lime characteristics to obtain a product of desired quality.

Slaked lime is produced by mixing quicklime with water. This hydration reaction



is highly exothermic releasing 27,500 BTU per Lb-Mole of CaO (20). The slaking process can be described as follows. When quicklime is added to water there will be a preliminary period during which the particles of lime absorb water into the pores with very slight hydration occurring. The small amount of heat generated during this period raises the temperature of the lime particles to a point where an increase in the temperature causes a rapid increase in the rate of hydration and rupturing of the particles. This causes the mixture of lime and water to rapidly reach to the boiling point. At this point, hydration proceeds at a rate independent of initial breaking of particles. Following this period of constant temperature, there will be a period during which a small amount of hydration of any previously unhydrated lime may take place, however the heat losses by radiation from the hydrator exceed the heat evolution due to hydration, causing a decrease in temperature. The peak temperature may occur within the first two minutes. Finally, the temperature drops more rapidly due to the cooling of the hydrator by radiation and convection to the surroundings (21). The reaction product in the hydrator will be a slurry consisting of discrete, micro-sized particles of Ca(OH)_2 and very little dissolved Ca(OH)_2 .

Efficient conversion of quicklime to hydroxide slurry is extremely important for FGD applications. Major variables exerting a profound effect on the quality of slaked lime are listed as below (22).

1. Reactivity of quicklime: Degree of burning (soft, hard or dead) influences the speed of slaking and temperature rise during slaking.
2. Particle size of quicklime: Finer size particles slake more rapidly. Adams (21) and Whitman et al. (23) pointed out that by using smaller quicklime particles, hydroxide slurry of finer particles can be obtained.
3. Amount of water: There are two extreme conditions which should be avoided. When excess water is used an adverse effect called drowning occurs. The rise in temperature will be low and slaking will be delayed. Incomplete hydration takes place resulting in coarser hydrate particles. On the other hand, if insufficient water is added to quicklime, excessively high temperature (400° - 500° F) will be generated, which may even dehydrate some of the lime that has initially hydrated. Due to lack of water to react, some unhydrated particles will result.
4. Temperature of water: Higher water temperature can shorten the slaking time.
5. Distribution of heat: Even distribution is required for a good slake, which is generally achieved by proper agitation in the hydrator.

Miller (20), in a detailed study on slaking aspects of lime, found that particle diameter of the resulting calcium hydroxide could be varied by selecting different slaking conditions. It is mentioned that the amount of heat developed and its distribution or dissipation controls the particle size distribution. A set of particle diameters and their specific surface areas were estimated for different slaking ratios (ratio of water to lime) and initial water temperatures. Experimental results in the above study showed that highest specific surface area was obtained at a slake ratio of 2.5 with an initial water temperature of 194° F. Specific surface area

decreased considerably at lower initial temperatures and higher slaking ratios. Miller (20) also calculated the initial temperature of water required to give a final slaking temperature of 212° F. These data show that any combination of slake ratio and temperature can be opted to produce a high specific area, as long as the final temperature is approaching but not exceeding 212° F. However, this temperature should be reached within thirty seconds. Miller (20) reported that a final slaking temperature of 212° F or above produces crystalline calcium hydroxide and the specific surface area of this suspension is greatly increased because of this crystallization. Miller's study deals with only two parameters, slaking ratio and initial water temperature. The possible effects of other parameters are not explained.

In the literature, slaking aspects of the FGD reagent preparation are seldom related to removal efficiencies. Surface area of lime slurry particles is of paramount importance since the dissolution to produce ions for reaction, occurs on the particle surface. Klingspor et al. (24) indicated that surface area of the sorbent has a major impact on the reactivity. As per them, the reaction rate can be enhanced by careful selection of slaking conditions. Ireland et al. (25) stated that finer particle size achieved during slaking will certainly help to provide maximum reactivity and thus lower stoichiometry in a spray dryer FGD application. Getler et al. (14) observed that maximum reactivity of Ca(OH)_2 is a function of the minimum elemental particle size obtained by proper slaking of a high surface area quicklime. They report that it is possible to produce discrete slurry particles with diameters below 0.5 microns by using a soft burned lime and right combinations of slake water temperatures, mixing equipment and water-lime ratio. This observation is similar to the one reported by Miller (20), however, it may not be practical to achieve the very small size particles just by varying slaking parameters.

In earlier years, there were some attempts made to show that hydrated lime exists in two different forms, a fine amorphous and a coarse crystalline, but this theory of two forms was also disproved (23). Hartman et al. (27) presented the structure of Ca(OH)_2 as amorphous

form only. A number of X-ray diffraction studies revealed a definite crystal structure for $\text{Ca}(\text{OH})_2$ which confirms its crystalline form (14). X-ray methods can be effectively used to study the degree of crystallinity in various substances (38). When a crystalline material is exposed to a beam of X-rays, the three dimensional array of atoms in the crystal scatters the electromagnetic radiation in such a way that the scattered waves from different atoms reinforce each other only in a certain direction. Relative intensity data obtained during this can be used to calculate crystallinity indices. Various researchers (29,30,31) used this technique for different clay minerals. Jozewicz et al . (32) applied a similar technique for FGD sorbents. They related normalized peak heights from X-ray diffraction patterns with B E T (Brunauer, Emmet, Teller) surface areas of a mixed dry $\text{Ca}(\text{OH})_2$ reagent used for FGD purposes. In their study, an increase in the peak intensity corresponded with the increase in B E T surface area and subsequent SO_2 capture. However, it is to be noted that in general, the width of the diffraction curve (measured at half of peak height) increases as the size of the crystal decreases, keeping everything else as same (64). This should result decrease in surface area with increase in normalized peak height. In a similar study (33) X-ray diffraction was used to detect the crystalline phases and sorbent utilization during dry injection removal of SO_2 from the flue gas.

The effect of water quality and water temperature on the slaking process has not been consistently demonstrated in the literature. Beals et al . (34) point out that calcium hydroxide yield will be reduced by nearly 30 percent by slaking with water containing high dissolved solids. It is also indicated that lime hydrate particles will be large resulting in smaller specific surface area. Fortune et al . (35) found that poor quality slaking water with high dissolved solids reacted with the surface of quicklime and blind the pores, preventing water infiltration, thus stopping the slaking process. Kirchgessner et al . (36) indicated that surface areas of hydrates made from soft- burned limes are at a minimum at 30^o C slaking temperature

while those made from hard-burned limes reach a minimum around 70°C. It is also noticed that a gradual increase in temperature of hydration water showed a clear tendency to produce hydrates having higher reactivity with SO₂. Ireland et al. (25) indicated that a reaction temperature of 180° F to 212°F generally is recommended to ensure complete slaking.

The above discussion leads to the conclusion that a good quality slaking water and an optimum slaking temperature are necessary for producing high reactive slaked lime. However, there are some contradictions reported in the literature. In a pilot plant test, Stevens et al. (37) investigated the effect of slaking water quality and slaking temperature on SO₂ removal. They tested normal, boiler blowdown and sulfate doped (with Total Dissolved Solids=1870 ppm) waters for slaking and found no significant difference in the spray dryer SO₂ removal. The particle size distribution of the slaked lime indicated that considerably larger particles are produced when lime is slaked with high sulfate water compared with either tap water or boiler blowdown water. In other words particle size didn't affect the performance of the reagent. This contradicts the effect of particle size on the removal efficiency as a recent pilot plant study by Norman (11) clearly showed that removal efficiency can be enhanced by decreasing the sorbent particle size. Also in the study (37), lime slaked at 175° F has given lower removal efficiency than at 160° F. Their study concludes that particle size may not be a contributing factor for removal efficiency, which contradicts various theories related to the removal mechanisms. Surface areas achieved are not reported in the study (37) which restricts any comparison with other studies in that aspect. Dharmarajan and Forbus (38) in another pilot plant study found no significant effect of slaking water temperature on product quality. Even temperatures as low as 52° F do not seem to affect the slaked lime quality, which is doubtful.

B. SPRAY ABSORPTION PROCESS FOR SO₂ REMOVAL:

In a typical spray dryer system, flue gas containing SO₂ enters at the top, at a temperature of about 350° F. Slaked lime-water slurry is pumped into a rotary atomizer with peripheral speeds of about 450 ft/sec. The atomizer creates droplets of about 50 microns in diameter. The droplet consists of discrete Ca(OH)₂ particles surrounded by water with some dissolved Ca(OH)₂. As the droplets contact with hot flue gas, evaporation and mass transfer phenomena with reaction occur simultaneously.

The drying behavior of a slurry droplet with freely moving sorbent particles can be expected to be similar to that of a solution droplet. As per the conventional drying theory (39) the evaporation from a slurry/solution droplet may be expected to occur in two stages. This approach of two stages has been adopted by various authors (6,26) to model the spray drying process. As per Getler et al. (26) the first stage exists from the time slurry enters the spray dryer until the particles just begin to touch each other and is called as 'constant rate' drying period. The second period takes off where the first period ended to a point where further evaporation ceases to occur. This is referred to as the 'falling rate' period. The first phase is of short duration and critical to the overall reaction whereas final reaction/drying occurs in the second phase. The basic steps involved during the above periods can be described as

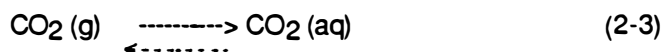
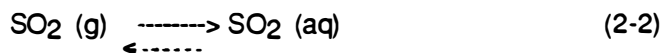
1. Reactants in the flue gas migrate into liquid droplets through random diffusion.
2. Chemical reactions occur in liquid phase. Turbulence and diffusion processes help promote these reactions.
3. Diffusion of reactants and reaction products occur through the pores of a particle system consisting of unreacted and reacted sorbent substances as well as reaction product.

During the first period, liquid droplets leaving the atomizer at high velocities around 450 ft/sec decelerated to velocities of around 30 ft/sec in less than 0.1 seconds. These droplets contain a large number of randomly moving, relatively insoluble, discrete particles. The inter-spacial distances between these particles will be several particle diameters. Through out this first phase, the water evaporation rate per unit area is high and constant (8). As the amount of water present in a droplet decreases due to evaporation, the size of the droplet decreases and the distance between discrete particles is reduced. Soon the particles contact with another. At this instance, the random motion of the particles is restricted. Diffusion through and around particles becomes the controlling factor.

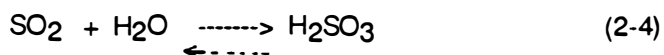
Ku et al . (8) suggested that the SO₂ absorption rate in the first drying period may have been controlled by the rate of mass transfer through the gas film surrounding the droplet or by the rate of mass transfer through the liquid film or by the rate of chemical reaction which neutralizes sulfur dioxide within the droplet. As per them, the controlling resistance is dependent on the concentration of sulfur dioxide. If the concentration is not relatively high, the droplet acts as a perfect sink and the absorption rate is totally gas-phase controlled. However, in an earlier study, Babu et al . (40) indicated that gas phase resistance is not significant for the absorption of sulfur dioxide (at 0.96 percent) in Ca(OH)₂ solution.

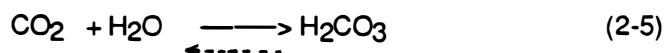
Various reactions that occur during the two drying periods can briefly be expressed in different steps as shown below (26). These reactions do not occur as single step but as a series of steps.

1 . Diffusion of SO₂ and CO₂ through the gas film boundary surrounding the droplet surface

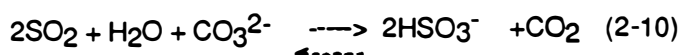
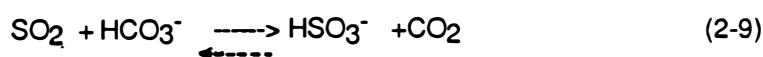
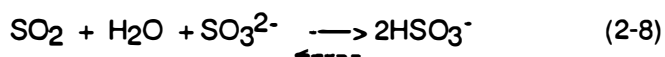
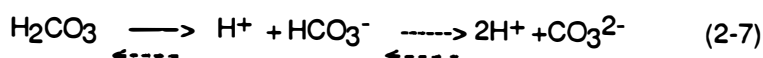
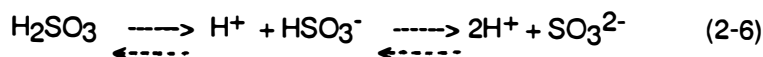


2. Dissolution of SO₂ and CO₂

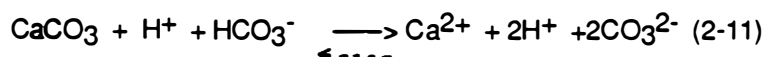




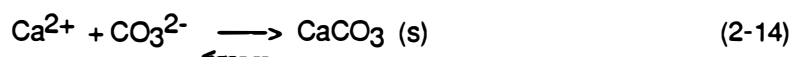
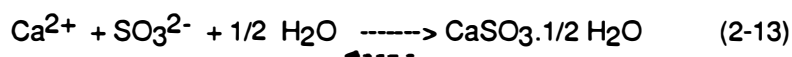
3. Dissociation in alkaline medium



4. Dissolution of solids



5. Formation of salts



The reactions in steps 2, 3 and 5 are believed to be rapid (therefore not rate controlling) and either gas diffusion or solid dissolution is the rate controlling step in the first phase (26). The instantaneous nature of sulfur dioxide absorption into calcium hydroxide solutions was also confirmed by Babu et al . (40). They estimated the enhancement factors experimentally, and found that they were fairly independent of contact time, from which, it was concluded that the reaction was instantaneous. Chang and Rochelle (41) explained this phenomenon using surface renewal theory. Their model fitted well with the experimental data, as compared with a previous model based upon penetration theory by Hikita et al . (42).

Klingspor et al. (24) believed that the formation of $\text{H}_2\text{O} \cdot \text{SO}_2$ complex was the rate determining step in the first period. During this complex formation sulfur atom is believed to be bound with the oxygen atom of a water molecule, which will displace the electron configuration around one of the hydrogen atoms. Thereby a reaction site in terms of a

positively charged hydrogen atom can combine with hydroxide to form intermediate and end products. This approach is different from the mechanism proposed by Getler et al. (26), and the rate controlling step in the first phase of the reaction is widely accepted to be either gas diffusion or solid dissolution.

The second phase starts when the particles in a droplet contact one another. The remaining moisture is removed as water diffuses to the surface. As the solubility limit is exceeded, a thin coating of powder will form on the particle surface. The drying rate is slow in this phase and it occurs by diffusion through the powder products and unreacted lime. During the falling rate period wherein the individual particles are no longer able to move, mass transfer takes place through the void volumes and interstices between elementary particles. Pore diffusion becomes progressively more important in this phase (26). The second phase is characterized by its falling rate of evaporation.

Getler et al. (26) estimated that approximately 75 percent water evaporation occurs before the falling rate period gets started. The basis for this (whether it is volume or mass) was not presented. At the starting of the second period, due to the restriction of particle motion, water paths become limited. Removal of remaining moisture will be more difficult. Diffusion through and around the particles will be the limiting factor in the second drying phase. Reaction continues as mass transport takes place through void volumes and interstices between elementary particles. In order to verify the surface reaction phenomenon, Getler et al. (26) performed Ca and S distribution analyses across the particle diameter with the help of SEM micrographs. It was found that Ca was distributed evenly across the diameter while the S content indicated a highly reacted particle surface and unreacted core.

Some calcium carbonate is formed during the above reactions. Previous studies (43) at The University of Tennessee pilot plant indicate that unreacted Ca(OH)_2 combines with CO_2 in flue gas to form CaCO_3 . As the mass transfer coefficient from air to water of SO_2 is

very high compared to that of CO₂ (44) it is thought that CaCO₃ is formed toward the lower part of the spray dryer where, assuming plug flow, most of the SO₂ has reacted and therefore the CO₂ concentration becomes the driving force. However, the concentration of CO₂ in flue gas is several magnitudes higher than that of SO₂ even at the entrance of spray dryer. The competition between SO₂ and CO₂ to react with Ca(OH)₂ is hardly discussed in literature. Kaplan and Felsvang (45) indicated that even though the partial pressure of CO₂ is 50 - 200 times that of SO₂, the product analysis has shown that only minor amounts of CO₂ are absorbed. The reason they point out is that SO₂ is a much stronger acid and will tend to drive off the CO₂. The Klingspor (46) study did not show any CaCO₃ in the product composition. The possibility of this reaction occurring with unreacted Ca(OH)₂ is however, not discussed by the author.

Governing equations for the wet particle stage can be developed by performing a rigorous analysis of heat and mass transfer balances and analogies. During the constant rate period, as the ionic reactions are very fast, it can be considered that overall rate of SO₂ removal is not controlled by these reactions. The other three important resistances for the transfer process are due to gas-film, liquid-film and dissolution of lime. The rate equations that apply for each of these resistances are presented below:

1. Gas-film resistance: Rate of SO₂ transfer by diffusion from the bulk gas phase to the droplet surface is given by (6)

$$N_S = k_d(\pi d_d^2) C (X_{g,s} - X_{d,s}) \quad (2-15)$$

where

N_S = molar rate of SO₂

k_d = gas-phase mass transfer coefficient

C = molar density

$X_{g,s}$ = mole fraction of SO₂ in bulk gas phase

$X_{d,s}$ = mole fraction of SO₂ at the droplet surface

d_d = droplet diameter

Mass transfer coefficients can be estimated by considering heat and mass transfer analogy. As per the correlations developed in the literature (6),

$$Sh = 2 + \hat{a} Re^{\beta} Sc^{\Omega} \quad (2-15 A)$$

$$Nu = 2 + \hat{a} Re^{\beta} Sc^{\Omega} \quad (2-15 B)$$

from which, it is established that under near zero relative velocity conditions, heat transfer to a spherical droplet can be expressed as (46)

$$Nu = 2.0 \quad (2-16)$$

From the analogy

$$Sh = 2.0 \quad (2-17)$$

In the above equations, Sh = Sherwood Number, Pr = Prandtl Number, Re = Reynolds Number, Sc = Schmidt Number and $\hat{a}$, β , Ω = Constants. Gas-phase mass transfer coefficient can then be obtained by

$$k_d = 2 D_{SO_2\text{-gas}}/d_d \quad (2-18)$$

where

$D_{SO_2\text{-gas}}$ = Diffusivity of SO₂ in flue gas

The effect of water evaporation on SO₂ diffusion can be incorporated into the above equation considering that the molar rate of evaporation of water, N_w , is much greater than N_s . Then the SO₂ transfer rate for non-zero surface SO₂ concentrations can be given as (6)

$$N_s = (X_{g,s} N_w/F-1) - (N_w X_{d,s} F/F-1) \quad (2-19)$$

where

$$F = \exp \left((N_w/2 \pi D_{SO_2\text{-gas}}) C d_d \right)$$

When molar rates of SO₂ and water are comparable eq. (2-15) will be the governing equation (6). The above equations are observed to be strongly dependent on SO₂ concentration in the bulk-gas phase.

2. Liquid-film resistance: The rate of transfer of SO₂ in the liquid phase from surface to bulk liquid is given by

$$N_S = k_l \phi \pi d_d^2 (C^*_{SO_2} - C_{SO_2,l}) \quad (2-20)$$

where

N_S = molar rate of SO₂

k_l = liquid phase mass transfer coefficient

ϕ = enhancement factor associated with the instantaneous nature of reaction

$C^*_{SO_2}$ = equilibrium SO₂ concentration at the droplet surface

$C_{SO_2,l}$ = bulk concentration of SO₂ in liquid phase

d_d = droplet diameter.

One of the approaches used to estimate the liquid phase mass transfer coefficient is to apply stagnant film model for the mass transfer. The film theory gives quite reliable predictions of the rate of mass transfer where there is a simultaneous chemical reaction, compared with the rate under the same conditions without reaction (47). By applying film theory

$$k_l = D_{SO_2\text{-water}} / \delta \quad (2-21)$$

where

$D_{SO_2\text{-water}}$ = Diffusivity of SO₂ in water

δ = film thickness.

Whenever a mass transfer operation is accompanied by an instantaneous chemical reaction, the mass transfer rate will be much higher than the one without reaction.

Enhancement factor will give the magnitude of this increase. In general enhancement factor is defined as (48)

$$\sigma = \text{rate with reaction} / \text{rate for mass transfer alone} \quad (2-22)$$

In case of the instantaneous reaction between slaked lime and SO_2 it can be expressed as

$$\sigma = 1 + (D_{\text{Ca(OH)}_2\text{-water}} C^*_{\text{Ca(OH)}_2}) / (D_{\text{SO}_2\text{-water}} C^*_{\text{SO}_2}) \quad (2-23)$$

where

D 's = diffusivities of slaked lime and SO_2 in water

$C^*_{\text{Ca(OH)}_2}$ = concentration of slaked lime in the bulk liquid

corresponding to its equilibrium solubility

$C^*_{\text{SO}_2}$ = equilibrium concentration of SO_2 in liquid phase at droplet surface

Also, for a fast reaction, both species will diffuse to a reaction front where their concentrations drop to zero, which suggests that $C_{\text{SO}_2,1}$ in eq. 2-20 becomes almost equal to zero. The final liquid phase rate equation thus becomes

$$N_s = k_l \sigma \pi d_d^2 C^*_{\text{SO}_2} \quad (2-24)$$

3. Dissolution of slaked lime: In a slurry droplet slaked lime dissolution rate is mainly dependent upon Ca(OH)_2 solubility in water, average inter-particle distance in the droplet and diffusivity of Ca(OH)_2 in water. The rate can be estimated using film theory as (6)

$$R_p = D_{\text{slaked lime-water}} \pi d_p^2 (C_l^* - C_l) / \delta \quad (2-25)$$

where

R_p = rate of dissolution for one Ca(OH)_2 particle

D = diffusivity

δ = liquid film thickness responsible for Ca(OH)_2 dissolution

d_p = Ca(OH)_2 particle diameter

C_1^* = equilibrium solubility concentration of slaked lime in water

C_1 = slaked lime concentration in bulk solution

Ca(OH)_2 dissolution from all the particles in a droplet can then be estimated as equal to R_p multiplied by number of particles in a droplet.

These equations assume a spherical shape for the slaked lime particle. The above approach suggests that for a given droplet size, dissolution rate can be increased by multi-fold, by having a smaller sorbent particle (i.e more number of particles in a droplet) and high specific surface area for these particles. The Ca(OH)_2 dissolution rate equations developed above ignore the effect of any product precipitation on to the sorbent particle.

C. MODELING OF SO_2 REMOVAL IN SPRAY DRYER:

Empirical and theoretical models have been developed by researchers to evaluate the performance of the spray dryer. Models will help to obtain information about the process performance and its relation to different variables without conducting extensive and expensive field or pilot tests. Empirical models may not always have sound theoretical background, yet are useful in predictions for a set of process conditions. Empirical models generally look into the mathematical relation between process variables or statistical occurrence of a particular variable or a set of variables. These models may have particular restrictions as far as the process conditions are concerned, because the models are developed from a particular set of data obtained by operating a particular process condition. Caution should be applied in using these models for a different scenario.

In the literature, the Log Model is often used to correlate the efficiency data. In this model, the log of fractional efficiency is assumed to be linearly proportional to the

stoichiometric ratio. Sometimes this is also presented in terms of penetration, i.e (1-efficiency) and stoichiometric ratios. These models assume that the remaining variables involved in the process are constant, which may not be true in all cases. The model also does not distinguish between different reagent methods. Babcock and Wilcox (50) represented the mathematical model as

$$E = 1 - \exp(-K(SR)) \quad (2-26)$$

where E is SO₂ removal efficiency fraction and K is a variable and a function of specific surface area of slaked lime and residence time of flue gas in the spray dryer. It was not indicated whether there was any procedure to calculate this variable for a given slaked lime and process condition. Test data are reported to fit very well for SO₂ concentrations of less than 2000 ppm and a close approach temperature. Downs et al . (49) used the log model to correlate the data from pilot studies. The model predicted well especially at low stoichiometric ratios (SR). The authors suggest that if adequate moisture remains (i.e if a close approach temperature is used) within the spray dryer, the model may be valid. Norman (11) compared the model with data obtained at The University of Tennessee pilot plant and found that if the model was forced to behave fairly well at higher SR's, the model crossed the perfect utilization line (a theoretical 100 percent sorbent utilization line) at lower SR values.

Farber (12) modified the log model to correlate the operating data obtained from a spray dryer FGD facility at Argonne National Laboratory. The relationship was presented as

$$SR = -\ln(1 - \text{Frac. removal}) / ((\text{inlet ppm of SO}_2 / 1000)(0.68 - 0.4 \text{ Frac. removal})) \quad (2-27)$$

Only fresh lime stoichiometric ratio values (referred to as external SR) were considered in this analysis. It was found that external stoichiometry was strongly influenced by the approach to adiabatic temperature and the above relationship was valid for 20° F approach temperature only. Neither regression coefficients nor graphical comparisons were given to check the

performance of the model. Bjerle et al. (62) related sorbent surface area empirically with removal efficiency as

$$-\ln(1-E) = K S_p SR t + B \quad (2-27 A)$$

where

E= Efficiency, fraction

K= Reaction rate constant, g/m² - sec.

S_p= Specific surface (BET) area, m²/g

SR= Stoichiometric ratio

t= Drying time

B= Constant

The above equation showed that reaction rate increases exponentially with BET surface area.

Babcock and Wilcox Co. (50) developed another mathematical model to characterize the reaction occurring during constant rate drying period. The model involved temperatures only as the parameters and was given as

$$E = 1 - ((t_p / (T_{in} - T_{sat}))^{0.62} \quad (2-28)$$

where

E= SO₂ removal efficiency fraction

t_p= approach to saturation temp., °F

T_{in}= inlet temperature of flue gas, °F

T_{out}= spray dryer outlet temp., °F

This model doesn't represent any parameters involving either sorbent quality or quantity. It was reported that the model was valid for relatively large spray dryers (greater than 8500 ACFM).

A generalized correlation between SO₂ removal and lime stoichiometry was obtained by Gustke et al. (51) as

$$SRE = (A/(SR + AA)) + B \Delta T + K \quad (2-29)$$

Where

SRE= SO₂ removal efficiency, percent

A,B= regression coefficients

SR= lime stoichiometric ratio

AA= ash alkalinity constant

ΔT = approach temp., °F

K= regression constant

The above relation was obtained after performing multiple regression analysis on 164 test data with different coals. The authors came up with a set of coefficients for each type of coal. The standard error estimate for the predictions varied between 3.9 to 9.1 percent. Similar to the previous models, this model doesn't use any input related to the sorbent characteristics. In the above model, the authors showed that stoichiometric ratio is inversely proportional to the removal efficiency, which is questionable.

In order to check the importance of constant rate period in SO₂ removal and to compare with the other two stages (falling rate and dry particle) Downs et. al (49) presented a model with an assumption that SO₂ absorption will be controlled only by gas phase diffusion during the constant rate period. The model was given as

$$N_T = (D_v / a) (N_{SH} / N_{Nu}) \ln((T_{in} - T_{sat}) / (T_{out} - T_{sat})) \quad (2-30)$$

where

N_T = number of transfer units for SO₂ absorption = $-\ln(1-E)$

E= SO₂ removal efficiency, fraction

T_{in} = inlet gas temperature, °F

T_{sat} = adiabatic saturation temperature, °F

T_{out} = outlet gas temperature, °F

D_V = mass diffusivity for SO_2 diffusion to droplet, ft^2/s

$\hat{\alpha}$ = thermal diffusivity to droplet, ft^2/s

N_{Sh} = Sherwood number for SO_2 absorption

N_{Nu} = Nusselt number for convection heat transfer

The above model had no specific provisions for the effect of lime stoichiometry as gas phase diffusion was assumed to control the constant rate period. When the model was applied to 20 data points it was observed that the model was underpredicting to a larger extent. From this, the authors concluded that the first reaction period, i.e constant drying rate period, was not the predominant zone for the SO_2 removal. This is contrary to the findings by other researchers (6,13). The conclusions that can be drawn from this are :

1. Gas phase diffusion is not the only mechanism that dominates at all times during constant drying period.
2. The approach used for calculating the mass transfer rates may be in error because, under continuous gas phase control conditions the model should overpredict as infinite capacity for SO_2 solubility and reaction is assumed to be present.

Chemical absorption processes with fast reaction into a slurry containing sparingly soluble fine particles have been studied by different researchers for Chemical Engineering applications. Ramachandran et al. (52) and Sada et al. (53) developed equations for different sets of conditions based on film theory, considering various resistances either in series or in parallel depending upon solubility in the liquid film. As spray drying process for SO_2 removal behaves on similar lines, efforts were made to extend the approach to model the SO_2 removal process.

Pearson (54) developed a model extending the two-film theory and using basic analytical equation derived by Ramachandran et al. (52). Two drying periods, constant rate and

falling rate are considered. The resistances which are considered to act in series are 1) gas film 2) liquid film 3) solid dissolution, and 4) ash film. A combined equation for the absorption flux accompanied by instantaneous reaction was developed. Contact times for each drying period were calculated using basic drying equations. The procedure adopted for the computations were handled well. This work showed that SO₂ removal in a spray dryer can be modeled using a mechanistic approach.

Damle (6) made an extensive effort to model the SO₂ removal process in a spray dryer. This model known as SPRAYMOD is developed under a contract to US EPA. In the model the overall process was divided into sub processes contributing to the SO₂ removal. Simultaneous heat and mass transfer processes were modeled in such a way that the model predicted the evaporation rate of a droplet and absorption / reaction of SO₂ with Ca(OH)₂ associated with the evaporating droplet. Drying of the droplet was considered initially to estimate the rate of drying and droplet moisture content with time, which provides an estimate of the total drying time for the droplet. The absorption and reaction of SO₂ in the droplet is analyzed to determine the rate of absorption / reaction and SO₂ removal during the droplet drying process. Two particle stages, wet and dry are considered for SO₂ removal process to occur. Wet particle stage is modeled considering gas phase, liquid phase and dissolution resistances acting in series as illustrated in Figure 2-1,

where

$X_{g,A}$ = mole fraction of SO₂ in gas phase

$X_{d,A}$ = mole fraction of SO₂ at gas-liquid interface

C_{Ai} = concentration corresponding to $X_{d,A}$

C_s = saturation solubility of Ca(OH)₂ in liquid phase.

Damle (6) used standard mass transfer equations (eq.'s 2-15, 2-20, 2-25) to arrive at the molar rates of SO₂ transfer for each of the three resistances. Citing an example with reasonable

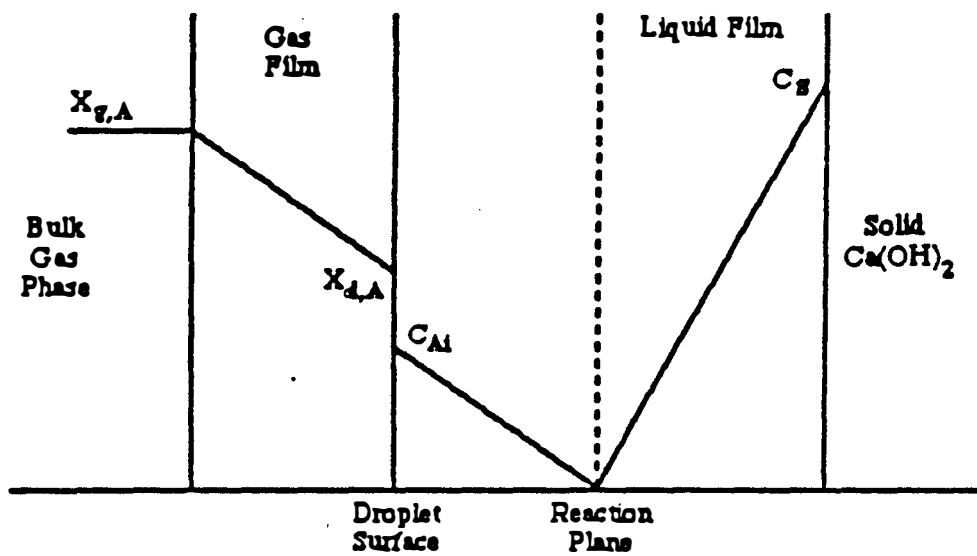


Figure 2-1. Damle model for wet particle stage.

values for different properties of the system, Damle (6) tried to determine the relative importance of gas-phase to liquid-phase mass transfer resistances. The conclusion was that gas-phase resistance was much higher than corresponding liquid-phase resistance in general. In other words liquid phase mass transfer was assumed to be a non-controlling factor in the overall SO₂ removal process. With this assumption, SPRAYMOD is developed such that at each time increment, the model calculates molar rates of SO₂ transfer based on gas phase and dissolution resistances, and compares the magnitude of individual rates to determine which resistance dominates. The mass transfer resistance, contributing to yield a smaller rate, controls the SO₂ removal rate for that time increment.

For the dry particle stage (starts when the moisture content approaches equilibrium moisture level) Damle (6) assumed a bulk volume reaction rate coefficient (KR) as a function of moisture content, to calculate the SO₂ removal rate. The molar rate (N_S) of SO₂ removal during dry particle stage is given by;

$$N_S = (KR \pi d_d^3 / 6) C_{SO_2,g} C_{remaining\ lime} \quad (2-31)$$

where

d_d = droplet diameter

$C_{SO_2,g}$ = gas phase SO₂ concentration

$C_{remaining\ lime}$ = concentration of remaining Ca(OH)₂, which varies with time.

SPRAYMOD is a well designed program that can handle both Na₂CO₃ solution and Ca(OH)₂ slurry operations in back mix and plug flow reactor options. Droplet evaporation aspects of heat transfer and system property correlations have also been handled very well. Damle (6) reported that model predictions compared with limited pilot plant data are within 10 percent of data values.

Davis et al. (55) compared SPRAYMOD predictions with pilot plant data collected over a period of time at the University of Tennessee pilot facilities. The predictions were observed

to be less sensitive to the effects of slurry concentrations and SO_2 concentrations, than the pilot data. It was expressed that the model predicting capability could be improved by following a rigorous approach in handling mass transfer calculations. Partridge (57) modified the model SPRAYMOD for the constant drying rate period (modified version is SPRAYMOD-M), by incorporating a mechanistic approach. It was found that neglecting liquid phase resistance was in error and a separate combined rate equation would improve the model. Partridge (57) developed a new absorption rate equation based on film theory with various resistances in series as shown in Figure 2-2. The approach used in considering these resistances was similar to a previous work by Maibodi et al. (56). The terms in Figure 2-2 are defined as follows: $X_{g,A}$ is the mole fraction of SO_2 in gas phase, $X_{d,A}$ is the mole fraction of SO_2 at the droplet surface, C_{Ai} is the concentration of SO_2 at the gas-liquid interface, C_B is the concentration of $\text{Ca}(\text{OH})_2$ in bulk liquid, C_s is the saturation solubility of $\text{Ca}(\text{OH})_2$ in the liquid phase, X is the distance from the gas-liquid interface and X_0 is the liquid film thickness.

The newly developed combined rate equation by Partridge (57) considered the resistances to act in series, similar to the earlier studies by Ramachandran (52) and Pearson (55), however a rigorous approach has been used in the development. SPRAYMOD-M calculates the molar rates based on 1) combined resistance equation, 2) gas film resistance, and 3) lime dissolution resistances and compares these rates. The smallest molar rate is considered as the control rate for that time increment. There is also a check at each iteration to determine if the resistance model is valid at those conditions. All the material and energy balance calculations from the original version are retained in SPRAYMOD-M, however some changes have been incorporated in determining the physical properties of the system and in the calculation of liquid film thickness. SPRAYMOD-M responded well to the slurry concentration and SO_2 concentration effects compared to the original model. The modified version predicted SO_2 removal efficiencies well in the 1000 - 2000 ppm SO_2 range and

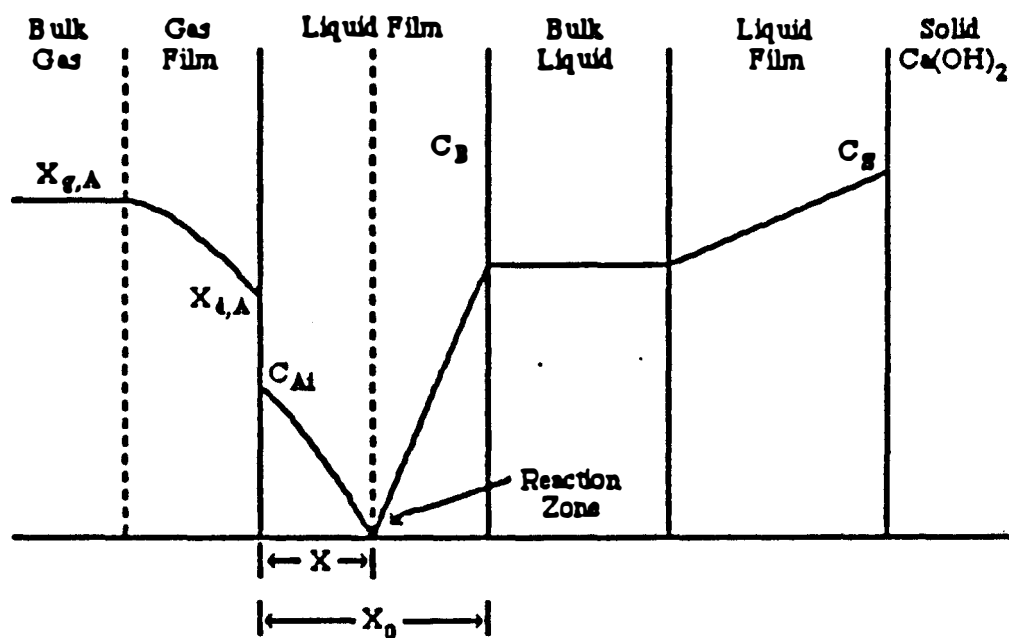


Figure 2-2. Partridge model for constant rate period.

exhibited a slight tendency to under predict at higher SO_2 and slurry concentrations (13). SPRAYMOD-M has certainly followed a rigorous approach in mass transfer calculations compared to the original version. However, the new model has some limitations. The model did not involve the entire SO_2 removal process. It addressed only the constant rate period of the wet particle stage. For the falling rate period, an empirical factor had been proposed so that the model can be carried into the dry particle stage.

CHAPTER III

EXPERIMENTAL PROCEDURES

The present work studied slaking aspects of different limes and performance characteristics of the resulting calcium hydroxide slurries. Slaking tests were done initially in the laboratory so that successful tests might be extended to pilot scale level. The reagent performance tests were conducted on a 1000 ACFM pilot scale facility located at The University of Tennessee's steam plant. Reagent characteristics were analyzed for particle size, specific surface area, X-ray diffraction and surface inspection by Scanning Electron Microscopy.

The laboratory slaking was performed in a stainless steel cylindrical vessel, fixed with an agitator and a thermocouple. A measured quantity of water at desired temperature was taken into the vessel initially and agitated continuously. The initial temperature of water was maintained at around 150° F. Different quality limes (CaO) obtained from Tenn-Luttrell Lime Company were tested. Some of these limes, which were in chunk form, were hammered to powder just before slaking. A determined amount of CaO was added to a pre-measured quantity of hot water to achieve a certain water to CaO ratio. Exothermic reaction between lime and water caused a rise in temperature of the mixture. The temperature of the mixture was noted at 10 second intervals up to 4 minutes. The temperature rise of the mixture was high initially, followed by a constant temperature period and then by a slow decrease in temperature. Once the slaking process was finished, the mixture was diluted by adding tap water and agitated thoroughly. Samples were taken at the end of each slaking test.

Performance tests for all the slaked limes were conducted at a pilot test facility. The pilot plant was constructed on a side stream of The University of Tennessee's stoker-fired boilers. A schematic diagram of the pilot plant is shown in Fig. 3-1. The facility consisted of a

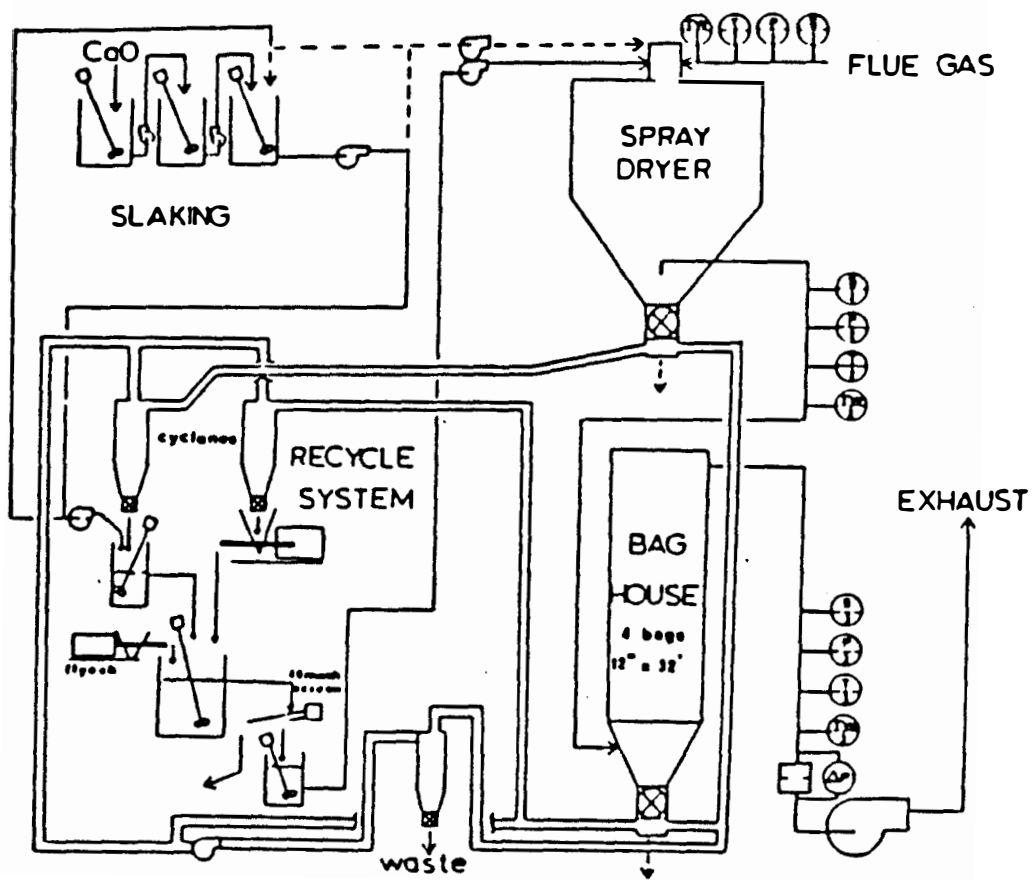


Figure 3-1. Schematic diagram of pilot plant.

slaking system control room, an instrument operating room, a 7 ft diameter spray drying chamber fitted with a variable speed Stork-Bowen AA-6 spray machine (5,000 - 21,000 rpm). This spray machine was equipped with a 6 in. diameter centrifugal atomizer with six nozzle inserts. For particulate control, the facility had a 36 bag collector provided with a pulse jet cleaning system. The bags were of 4.5 in. X 12 ft. size and made of fiber glass. There were provisions for solids recycle also. A continuous pneumatic recycle system was available to partially convey the products from the bag house and spray dryer into a feed tank which pumps slurry into the atomizer. The bag house was periodically cleaned as required to minimize pressure drop across the bag house.

The slaking room consisted of three 55 gallon tanks provided with agitators and transfer pumps. One of the tanks served as the lime hydrator and was equipped with a thermocouple to measure the temperature during slaking process. The slaking procedure followed was similar to the laboratory method, but at a larger scale. When slaking was finished, part of the slaked lime was transferred to a final feed tank. The slurry was diluted as per the test conditions and then titrated to a phenolphthalein end-point using standardized 3.0 N HCl to determine the available CaO. Further dilution to the desired concentration was made if necessary, and a final titration was performed. The slurry was screened through a 420 micron vibrating screen prior to the delivery to atomizer, in order to prevent clogging of the slurry lines and atomizer nozzles. The slaked lime slurry was continuously recycled between the slaking room and spray dryer input control room so that plugging in transport lines could be avoided. A pump which draws from this recycle line supplied slurry into a continuously stirred, constant level tank. The level in the tank was maintained at a constant level with the help of a float valve. This procedure was adopted to ensure that the atomizer receives the specified flow at all times. The slaked lime slurry flow rate into the constant level tank was used to calculate stoichiometric ratio for a given set of operating conditions. Makeup water was added to

maintain the level in the tank as well as to obtain desired approach to saturation across the spray dryer. The addition of makeup water is not believed to be a major contributor for changes in the surface characteristics of the slaked lime slurry, as the laboratory techniques to measure these characteristics, also involve large extent of dilution. In the industrial application also, desired approach to saturation temperature in the spray dryer is achieved by adding adequate amount of water to the slaked lime slurry before atomization. In this study, slaked lime slurry (excepting the ones pretreated with grinding) was tested within two hours after slaking, similar to industrial practice. In the case of slaked limes involving delayed testing, pilot plant tests were also made with a 'control' slurry (a portion of slurry retained at pilot plant during off-site grinding operation) both before and after the grinding operation.

System instrumentation provided for continuous monitoring of temperature, SO₂ concentration and static pressures at the inlet and outlet of both spray dryer and bag house. Sampling locations for these are indicated in Fig. 3-1 by the symbols T, S and P respectively. Volumetric flow rate was measured through an orifice plate. Gas samples were extracted through heat trace lines (to prevent any possible condensation) for SO₂ analysis. There were provisions for two Lear-Siegler SM 810 analyzers, a TECO model 800 - model 40 gas conditioner / analyzer and one Westinghouse SO₂ - O₂ analyzer for measuring SO₂ concentration. Depending upon the availability of analyzers, multiple or individual ports were analyzed sequentially. Wet bulb temperatures were measured by a hand-held wetted wick thermometer. Spray dryer inlet temperature was generally controlled by a dilution air damper located up-stream of the sampling port of spray dryer inlet. Supplemental injection of SO₂ was made to obtain desired concentration at the spray dryer inlet.

In general, it took about an hour to reach a stable inlet temperature of 300° F. During this time, lime slaking operations were performed and desired slurry concentration was obtained. After achieving operating approach temperature across the spray dryer and desired

inlet SO₂ concentration at the inlet of spray dryer, monitoring of the system was started. Each test condition was run for about an hour (at least). Each test point calculation consisted of monitoring 18 different parameters which includes SO₂ concentrations at three different locations (ports 1-3), various temperatures, Ca(OH)₂ slurry flow rate, available CaO (by HCl titrations). The air leakage rate through the system and sample lines was conducted periodically and corrections were applied accordingly. After each test, slurry sample and products from spray dryer and bag house were collected and analyzed in the laboratory for different characteristics.

In addition to the regular slaking tests, some tests with slurry reagent pretreated by grinding were also conducted. The main aim in grinding the slurry was to obtain a very small sorbent particle size. The grinding operation was done in a vertical tower mill located at Atlantic Research Company, Alexandria, Virginia. The tower mill consisted of a vertical screw (with wide vanes) rotating in clockwise direction (viewed from top) in a cylindrical shell. The equipment (type Kw-10) was supplied by 'Koppers Company' and had a typical grinding charge of two tons of 1 inch forged steel grinding balls. The screw was running at an r.p.m of 84 with the help of a step down gear box and 10 HP electric motor. The grinding mill had a provision for continuous cycle, however grinding was done on batch-wise in the present testing. Typically, feed slurry entered from the top and the product was drawn from the bottom.

In the present testing, Ca(OH)₂ slurry was ground to two different particle sizes. Settling tests were done periodically with samples drawn at different time intervals, just to obtain an approximate particle size. Grinding was performed for about three days to obtain two drums of slurry (55 gallons each) with two different particle sizes. The slaked lime slurries were brought to pilot facilities as soon as possible and tested for performance.

Various laboratory tests were performed to analyze the characteristics of quick lime, slaked lime slurries and reaction products. The particle size distribution of slaked lime slurries and reaction products were determined by using a COULTER COUNTER (58). This instrument determines the number and sizes of particles suspended in conductive liquid by forcing the suspension to flow through a small aperture. Electrodes are immersed in the conductive liquid on both sides of the aperture. As a particle passes through the aperture, it changes the resistance between the electrodes. This produces a current pulse of short duration with a magnitude proportional to the particle volume. The instrument monitors the electrical current pulses and electromagnetically scales and counts the number and size of the particles. In the present work, 5 percent lithium chloride in methanol solvent was used as the electrolyte. The accumulated distribution obtained from the counter was plotted on log-linear paper. In general, the distribution was found to follow a "S-shaped" curve. The characteristic particle size was chosen to be represented by 'number mean diameter'. This represents that diameter at which the number of all particles larger (or smaller) than that diameter constitutes 50 percent of the total number. This characteristic diameter was determined by drawing a line from 50 percent cumulative percent line on to the curve and obtaining the corresponding diameter from the other axis. Figure 3-2 shows a typical curve obtained from the instrument. By considering a single diameter from this curve, it may indicate that some larger and smaller (than the size considered) diameters are not taken into the analysis. However, it is to be noted that the shape of the curves for all the measurements remained same through out this work and the geometric standard deviation values were found to be consistent. A relatively accurate estimation for the contribution of larger (or smaller) particles for the average surface area, can be made by analyzing a known mass of Ca(OH)_2 slurry. In this study, such attempts were not made as the surface area was measured by other techniques.

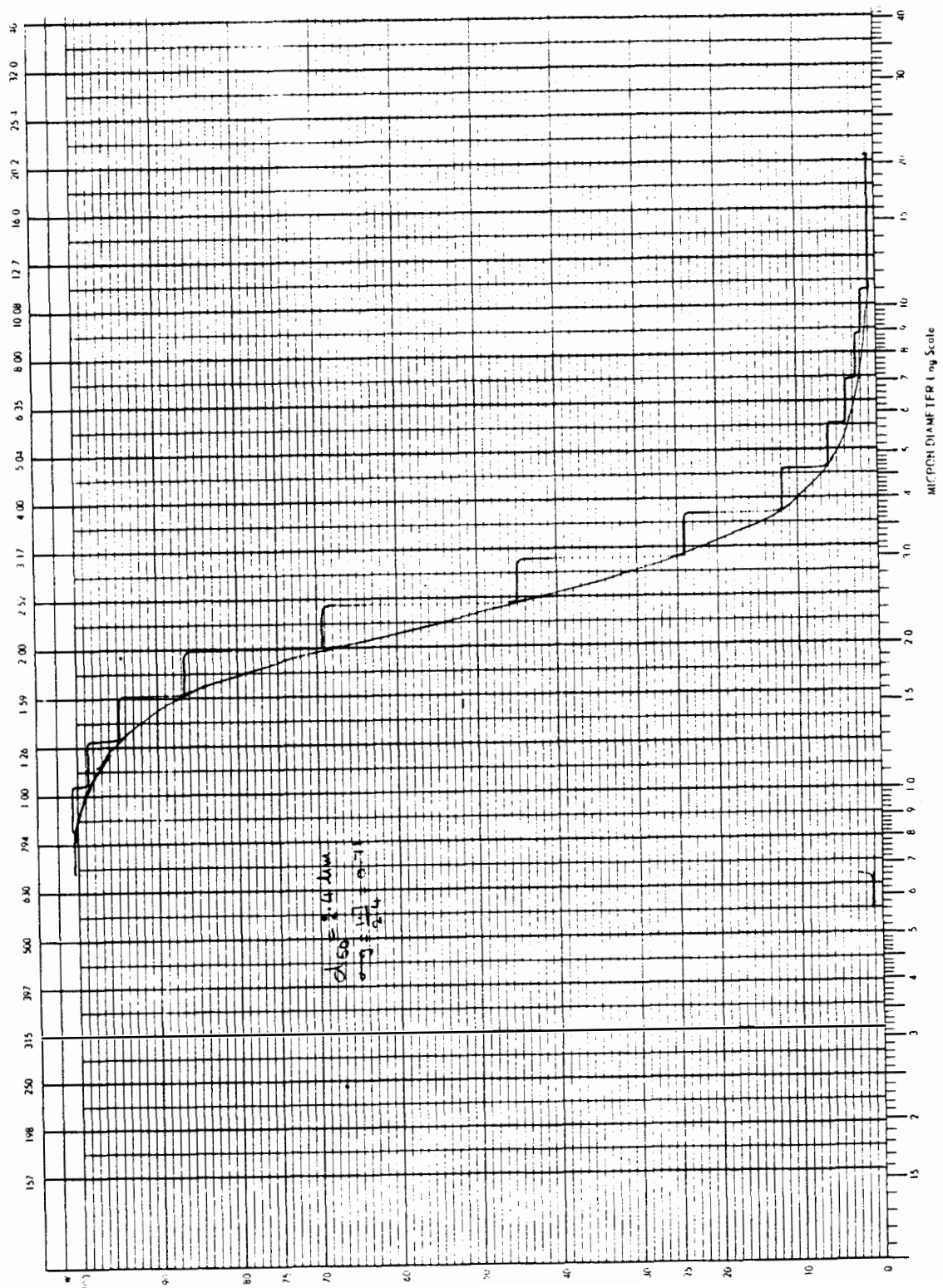


Figure 3-2. Sample curve for particle size measurement.

Surface area of slaked lime slurries and product particles were determined with the help of a ' MICROMERITICS ' (model no. 2200) surface area analyzer. This instrument measures the surface area by determining the quantity of nitrogen gas necessary to form a single layer (mono molecular layer) on a representative sample. The corresponding surface area is then evaluated using the modified B-E-T equation (59). The dry powder was obtained from the solution by filtering onto a filter paper (forming a thin coating) and letting it dry in a vacuum desiccator. S E M micrographs for slurry samples were made at the facilities located in Material Science and Engineering department at The University of Tennessee.

In the present work, X-ray diffraction studies were performed on a ' Philips ' diffractometer (model D4 1314) located in Geology department at The University of Tennessee. X-ray diffraction furnished a rapid, accurate method for the identification of crystalline phases present in a material. The X-ray equipment was operated with packed mounts for powder samples and elutriated slides for slaked lime slurries. The degree of crystallinity for lime slurries was evaluated and compared by calculating the normalized peak heights of diffraction patterns.

CHAPTER IV

RESULTS AND DISCUSSION

The present work looked into different aspects of lime slaking and their effect on the SO₂ removal efficiency in a FGD spray dryer. A previous study (11) conducted at a SO₂ concentration of 1000 ppm showed that a near stoichiometric lime utilization in a spray dryer could be achieved by opting either a special slaked lime or a conventional slaked lime with very small particle diameter. Based upon this above study, the present work aimed at checking the applicability of the previous approach for obtaining high SO₂ removal efficiencies for systems involving high inlet SO₂ concentrations, typically evolved from boiler stacks using high sulfur eastern coals. As indicated earlier, the surface area and particle size of sorbent particles play a vital role in obtaining higher SO₂ removals. This study made an attempt to relate these parameters with the sorbent performance in removing SO₂ across a spray dryer. Empirical and theoretical models were used in this work to explain the effects of various slaking parameters on the removal efficiency.

A. STUDIES WITH MODIFIED LIMES:

In an earlier study Norman (11) achieved 96 percent SO₂ removal (at 1000 ppm level) across a spray dryer using "hot lime". This lime was obtained by following special procedures in production / handling of the manufacturing process. In the manufacture of lime, there are two places at which quicklime is exposed to air. They are 1) air quenching after leaving the kiln and 2) storage bins after crushing. In the previous study (11) hot quicklime leaving the kiln was collected and stored in a sealed container so that its temperature was decreased by radiant cooling, minimizing the exposure to air. These aggregates were crushed just before the

slaking operation. The slaking process using this lime was found to be very violent, reaching the boiling point in only 13 seconds. Very high removal efficiencies were obtained with this slaked lime compared to the slaked lime processed in conventional manner. In the same work, another lime called 'air quenched' lime which was obtained before the crusher (after the cooling operation) was also studied and the resulting Ca(OH)_2 slurry was reported to be more reactive than the conventional lime (referred to as 'regular lime') derived hydroxide slurry. The high reactivity of these slaked limes was thought to be achieved due to very limited exposure of CaO to air. Regular quicklime because of its extended exposure to carbon dioxide and moisture in air (in air quenching and crushing operations) was anticipated to form a layer of CaCO_3 around each individual particle. These layers on all particles were thought to be the reason for a comparatively slow $\text{CaO} / \text{H}_2\text{O}$ reaction associated with the regular lime. The study (11) also looked into the aspects of decreasing sorbent particle size for attaining higher efficiencies. It was concluded that a near stoichiometric reaction in the spray dryer was possible with either a special slaked lime having high surface area or regular slaked lime with very small particles (close to 1 micron). The present work made an attempt to extend the previous approach for high SO_2 concentration and to find out the limitations involved.

Earlier research (26) showed the importance of surface area in achieving high SO_2 removals. Norman's study (11) pointed out that surface area was the contributing sorbent property for the high removals achieved but, attempts were not made to measure sorbent surface area that could be related to the performance. In the present study, laboratory scale slaking tests were performed and tested for their surface area. Specific surface areas for the vacuum dried slurry samples were measured using a surface area meter. Earlier work by Norman (11) and Miller (20) indicated that high surface area Ca(OH)_2 was achieved by crystallization during slaking process. In order to check this effect, estimates for crystallinity indices were made in the present study, using X-ray diffraction peak analysis. The crystallinity

index was calculated as the ratio of peak height to the peak width at half of the peak height. Three major peaks from each pattern were considered and the average ratio was reported as the crystallinity index. There were some unidentified peaks in the diffraction patterns which were considered as insignificant due to their small peak heights. Particle size measurements were also made using a Coulter Counter. Average values obtained for crystallinity indices, specific surface areas and particle diameters, for different slaked lime slurries are presented in Table 4-1. It is observed that the specific surface area value for $\text{Ca}(\text{OH})_2$ has increased from regular lime to hot lime. This increase corresponds with the change in crystallinity also. No direct relation can be drawn from these two parameters because crystallinity indices are only qualitative parameters but not absolute values. Interestingly, the particle diameters do not follow the pattern of smaller size for larger surface area. This suggests that particles from different slaked lime slurries may have different shapes. The crystal morphology of CaO is of a cubical pattern whereas calcium hydroxide crystallizes into a hexagonal - rhombohedral system (14). In other words during the slaking process the crystal morphology is changing from cubical pattern to hexagonal - rhombohedral system. The degree of crystallinity may be an indicator for the calcium hydroxide recrystallization process as proposed by Miller (20). In order to distinguish the differences in the resulting slurry particle, S E M micrographs were made for the slaked products of regular lime and hot lime. These are presented in Figure 4-1 and Figure 4-2 respectively for $\text{Ca}(\text{OH})_2$ obtained from hot lime and regular lime. The micrographs did not show any major differences in the crystal morphology. The above were only preliminary laboratory tests and no performance tests were conducted with these slaked limes. As such, the results couldn't be linked with any SO_2 removal efficiencies across the spray dryer. However, an earlier study by Jozewicz et al. (32) successfully linked changes in sorbent diffraction patterns with its surface area and subsequent SO_2 removal efficiency.

Table 4-1. Experimental values for different Ca(OH)_2 slurries slaked in laboratory during the present study

QUICKLIME USED FOR SLAKING	CRYSTALLINITY INDEX	SP.SURFACE AREA m^2/g	PARTICLE SIZE μm
Regular lime	43.3	22.60	3.47
Air quenched lime	62.0	28.58	4.43
Hot lime	68.4	29.10	3.62



Figure 4-1. SEM micrograph for Ca(OH)_2 from hot lime slaked in laboratory, 5000 X, magnification.

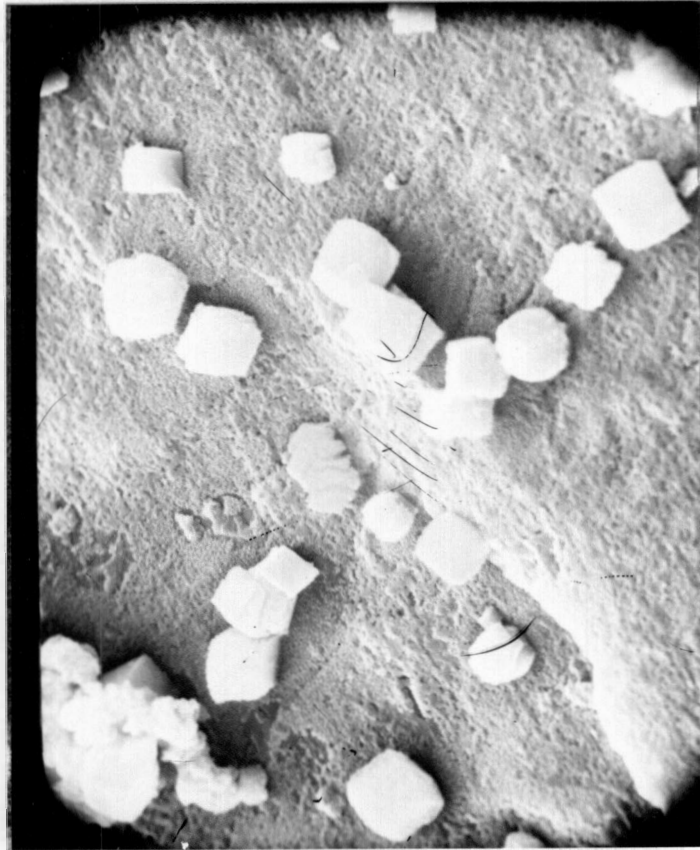


Figure 4-2. SEM micrograph for Ca(OH)_2 from regular lime slaked in laboratory, 5000 X, magnification.

Norman (11) in an earlier study on hot lime concluded that exposure of regular quicklime to atmospheric CO₂ and moisture (forming CaCO₃) during manufacturing process, was a possible reason for the low reactivity of its slaked product. In order to check the extent of carbonate presence in regular lime, X-ray diffraction technique was used to identify the carbonate peaks. Sample of quicklime from storage drums at the pilot facilities was tested. The diffraction pattern did not yield any carbonate peaks. It matched exactly with the standard pattern for calcium oxide, confirming the non-existence of carbonate in the regular lime, manufactured in a conventional manner by Tenn - Luttrell Lime Company. However, quicklime exposed to an atmosphere of moderate to high relative humidity was reported to be ' air-slaked ' and subsequent CO₂ absorption by the resulting hydroxide was also noticed (14). In the present study X-ray diffraction tests conducted on a sample exposed to the atmosphere for several days, showed the presence of carbonate. These studies show that carbonate formation during manufacturing process is possible only when very high moisture is present in the quench air. In a normal operation, there is very little possibility for the carbonate formation. It is to be noted that there were some unidentified peaks in the diffraction patterns, but these peak heights were found to be relatively insignificant.

In order to extend the hot lime tests for high SO₂ concentrations, lime samples from the kiln were collected and sealed immediately, following the procedures described in the earlier study (11). The lime aggregates were crushed just before the slaking operation. The slurry was tested for SO₂ removal across the spray dryer at the following conditions: Inlet SO₂ concentration - 3000 ppm, approach to saturation temperature - 300° F, and stoichiometric ratio - 1. It was found that Ca(OH)₂ slurry obtained from hot lime did not yield removals near stoichiometric utilization, but the performance was similar to regular slaked lime reported in earlier studies (57). In order to recheck the above finding, another batch of Ca(OH)₂ slurry from hot lime was tested at the same conditions. The removal efficiency was only around 40

percent just as the above. This led to a conclusion that, Ca(OH)_2 slurries from regular lime and hot lime (tested in this study) were no different as far their reactivity was concerned. In order to verify this conclusion, pilot plant tests with another batch of slaked lime slurry from hot lime were conducted at conditions similar to previous study (11) i.e at inlet SO_2 concentration of 1000 ppm and approach to saturation temperature of 20°F . It was observed once again that Ca(OH)_2 slurries from hot lime and regular lime behave similarly. Pilot tests with regular slaked lime were conducted immediately in order to check the total system and its response. The pilot system behaved similar to earlier regular slaked lime tests. Specific surface area and crystallinity index values for Ca(OH)_2 slurries obtained from hot lime samples were compared with the laboratory samples as shown in Table 4-2. The surface area values did not follow a particular trend, however the crystallinity indices for Ca(OH)_2 slurries (from hot lime) tested in the pilot plant were found to be lower than the value obtained with the laboratory hot lime sample. Generally in a diffraction curve, as the peak width increases with decrease in crystal size, higher index values should reflect smaller surface areas. However, this trend is not observed in the present study. As the index for the slaked lime (obtained from hot lime) tested in the previous study (11) (with high SO_2 removal efficiencies) was also found to be smaller than that of the lab sample in this study, any link between removal efficiency and crystallinity index could not be confirmed. Pilot plant efficiency data from the three different batches of slaked limes (obtained from hot lime) in this study, were not found to be closer to any of the previous study's (11) data. Hot limes in this study and previous study might have been processed at different calcination conditions. These conditions were not closely monitored in both the studies, and so, no positive conclusions could be drawn from this. One observation that was quite different from the previous study, was the violent nature of the slake. It was noticed that hot lime in the previous study took only 13 seconds for a complete

Table 4-2. Comparison of experimental values for crystallinity indices and surface areas for different slaked limes.

STUDY	LIME USED FOR SLAKING	CRYSTALLINITY INDEX	SP.SURFACE AREA M ² /G
Present study - Lab samples	Regular lime	43.3	22.60
	Air quenched lime	62.0	28.58
	Hot lime	68.4	29.10
Present study- Pilot plant	Hot lime I	44.3	26.87
	Hot lime II	49.0	32.58
	Hot lime III	45.0	-
Previous study- Pilot plant (11)	Hot lime	53.2	30.46

slake and the process was observed to be a very violent reaction. In the present study, no such observations were found.

In a separate study (60) removal efficiencies around 90 percent were reported across the spray dryer, using promoters. Significant removal improvements were obtained by mixing calcium chloride salts (up to 10 percent) with the lime slurry. Higher removal rates due to the promoter salts were linked to the ability of salts in retaining moisture. Kinzey and Harriott (61) reported that even with a low initial salt concentration, SO₂ absorption could be continued further as evaporation concentrates the salt solution and a significant amount of water would be retained. Additional removal of SO₂ was linked to the extra SO₂ absorbed in the larger pool of retained solution. Higher efficiencies attained in Norman's study (11) may be due to the presence of any foreign material in the original limestone or quicklime, that might have been carried over to the slaked lime. As indicated above, even low concentrations of some salts can enhance the removal efficiency. The present study did not conduct any tests with salts and so, this phenomenon could not be confirmed. Slaked lime samples of hot lime used in the previous study (11), was analyzed through X-ray diffraction and it did not show the presence of any compounds other than Ca(OH)₂ and CaCO₃.

B. EFFECT OF PARTICLE SIZE/SURFACE AREA:

One of the parameters of slaked lime, directly linked to removal efficiency was its particle diameter. The present study involved grinding of slurry obtained after regular slaking operation and testing the resulting slurries at the pilot facilities. The grinding operation was performed in a vertical tower mill at the facilities of Atlantic Research Company in Alexandria, Va. Lime slaked at a ratio of 3.4, generally yields a particle diameter of around 3.5 microns. The grinding operation was planned to obtain two different slurries with particle diameters of around one micron and two microns. Grinding was done for about three days to obtain two 55

gallon drums of slaked lime. The lime slurries were brought to the pilot facilities as soon as possible and tested for performance. The operating conditions were as followed: Inlet SO₂ concentration - 1000 ppm, Inlet flue gas temperature - 300^o F, and approach to saturation temperature - 20^o F. Average values obtained for the particle sizes and removal efficiencies with different particle sizes at various stoichiometric ratios (SR), are presented in Table 4-3. The pilot plant efficiency values were obtained from a three run average, with test conditions maintained very close to each other. Regarding the particle diameters, 2.4 um value was an average of seven Coulter Counter runs, with a standard deviation of 0.12. Second diameter 2.7 um, was also an average of seven runs with a standard deviation of 0.19 and 3.4 um value for the other diameter was average of nine runs with a standard deviation of 0.48. Comparison of the efficiency values for the three slaked limes at around 1.0 SR, shows a marginal increase from 3.4 micron particle to 2.4 micron particle slurry. This indicates the trend of increase in efficiency with decrease in particle size. Spray dryer removal efficiencies plotted against the stoichiometric ratios are shown in Figures 4-3, 4-4 and 4-5 respectively for 2.4 micron, 2.7 micron and 3.4 micron particles. The dashed lines indicate the 100 percent sorbent utilization lines. Figure 4-6 represents all the data obtained for the three slaked limes. These figures show that the test conditions for each slaked lime included the possible scenario for obtaining maximum efficiency. Referring to Figure 4-3, for 2.4 micron slaked lime, the efficiency curve is almost flat after 1.0 SR, which indicates that maximum possible efficiency is reached at around 1.0 SR value and any further increase in Ca(OH)₂ input has practically no effect on the removal efficiency. Theoretically the efficiency should be close to 100 percent at 1.0 SR for perfect utilization. If that is not the case, the efficiency values should show an increase with additional input of Ca(OH)₂, i.e at higher stoichiometric ratios. However, in the present case, this trend has not been observed. This concludes that slake lime with 2.4 micron particles has achieved its maximum utilization, which is around 80 percent and no further increase is

Table 4-3. Average pilot plant data for different slaked lime slurries.

S R	S.D REMOVAL EFF. %
<u>2.4 MICRON Ca(OH)₂</u>	
0.50	48.5
0.97	76.9
1.29	75.9
1.62	76.2
<u>2.7 MICRON Ca(OH)₂</u>	
0.48	47.7
0.97	73.1
1.82	78.6
<u>3.4 MICRON Ca(OH)₂</u>	
0.9	68.3
1.5	74.9
2.3	74.4

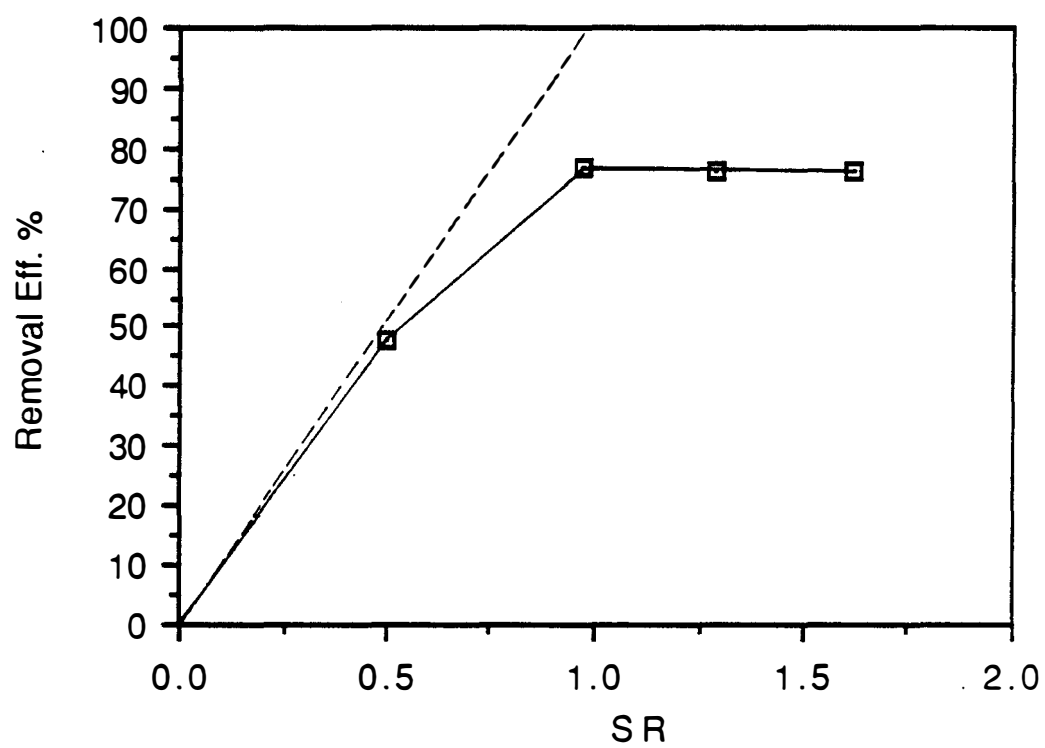


Figure 4-3. Spray dryer removal efficiency vs. stoichiometric ratio for 2.4 micron slaked lime.

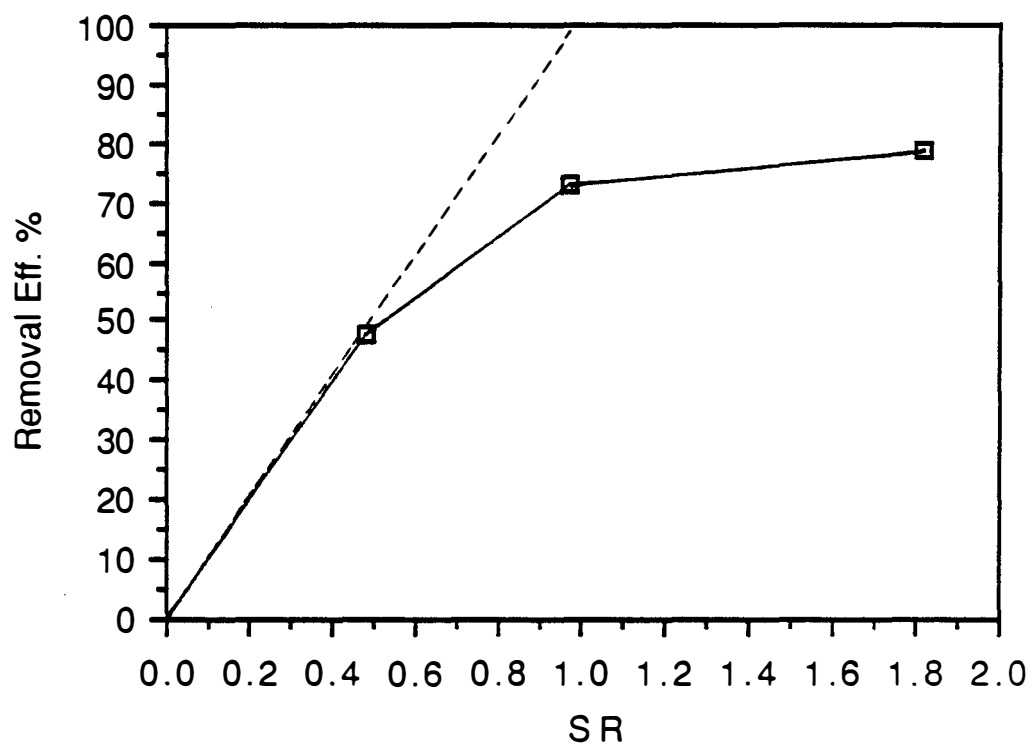


Figure 4-4. Spray dryer removal efficiency vs. stoichiometric ratio for 2.7 micron slaked lime.

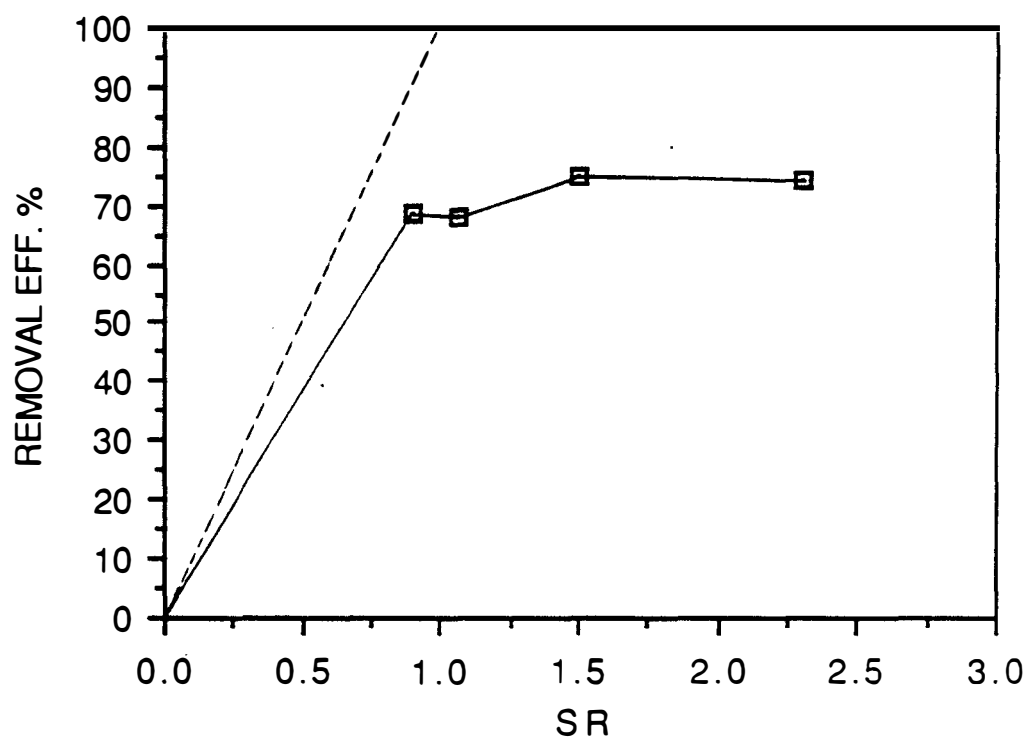


Figure 4-5. Spray dryer removal efficiency vs. stoichiometric ratio for $\text{Ca}(\text{OH})_2$ with 3.4 micron particles.

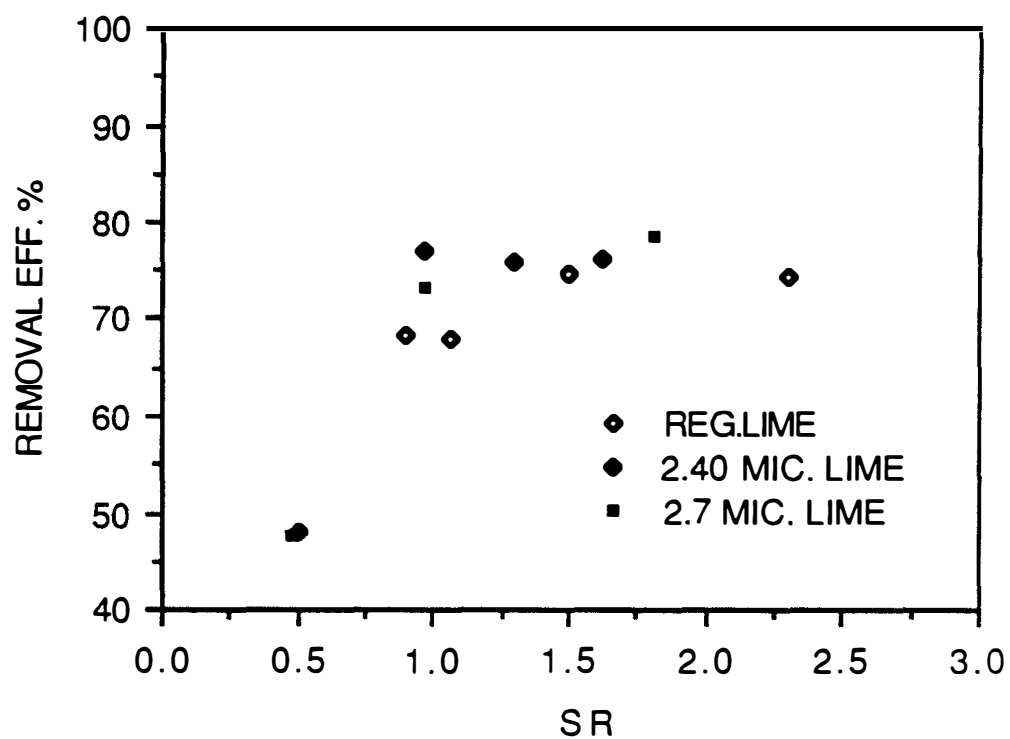


Figure 4-6. Spray dryer removal efficiency vs. stoichiometric ratio for the three slaked limes.

possible for this slurry at the conditions in which the system is operated. The other two slaked limes showed utilizations of about 75 and 70 percent respectively for 2.7 and 3.4 micron particle sizes. The plots for the three slaked limes also indicate that removal efficiency is not a function of stoichiometric ratio alone. They suggest that slurry preparation and particle diameter achieved during slaking process can affect the performance of a slurry.

In order to visualize the effect of particle diameter on spray dryer removal efficiency, some data (at larger particle diameters) at similar conditions from a previous study (11) are combined with the present data. In all the figures, the trend lines are represented by dashed lines. Figure 4-7 shows the trend of removal efficiency varying with particle size at a stoichiometric ratio of around one. The data did not yield a straight line plot showing that efficiency is not a linear function of particle diameter. This suggests that other characteristics of the particle might have been involved. As indicated earlier, previous researchers related surface area with efficiency. In order to compare different slurries, specific surface area (surface area for unit weight or volume) can be conveniently used. In the absence of such data, reciprocal values of diameters, (which translates into specific surface area on spherical particle basis) often present an equivalent comparison. Figure 4-8 shows the trend obtained for different particle sizes at a stoichiometric ratio of one. The straight line nature of the plot indirectly confirms the dependence of removal efficiency on the specific surface area provided by the slaked lime particle. It is obvious to conclude that reciprocal of particle diameter is a better variable to compare than a direct value of the diameter, for assessing the performance potential between two different slurries.

The present study also involved the measurement of specific surface area (B E T surface area) of different slaked lime slurries indicated above. Figure 4-9 presents the relationship obtained, between specific surface area of Ca(OH)_2 particles and corresponding sorbent particle sizes. This provided an opportunity to directly link the measured surface area

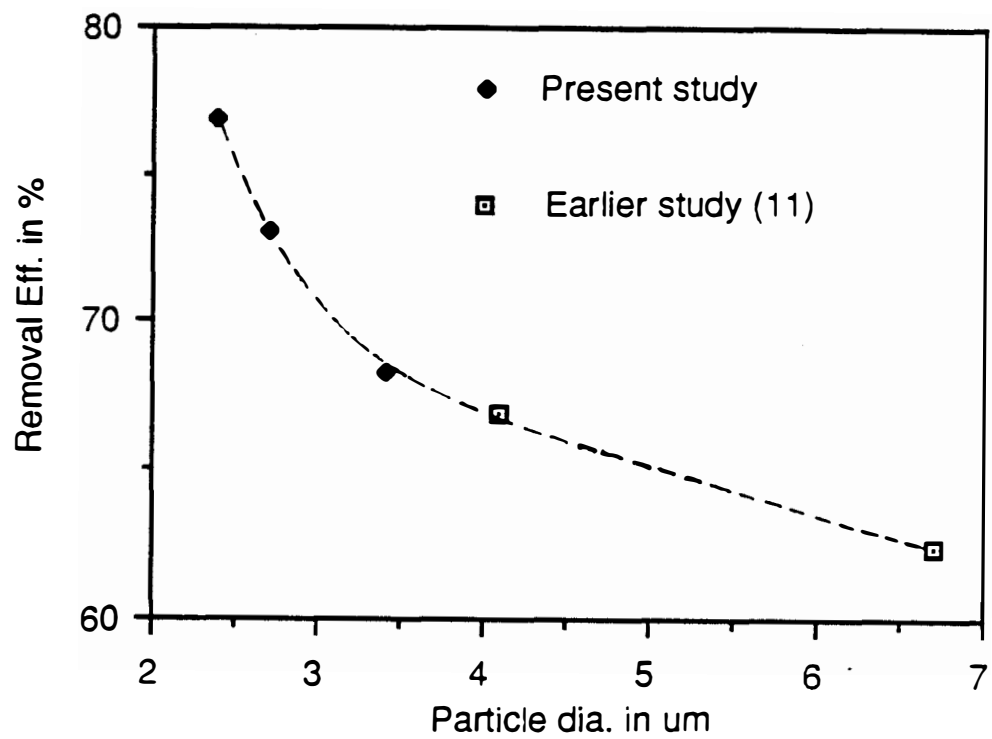


Figure 4-7. Particle size vs. removal efficiency at $\text{SR}=1$.

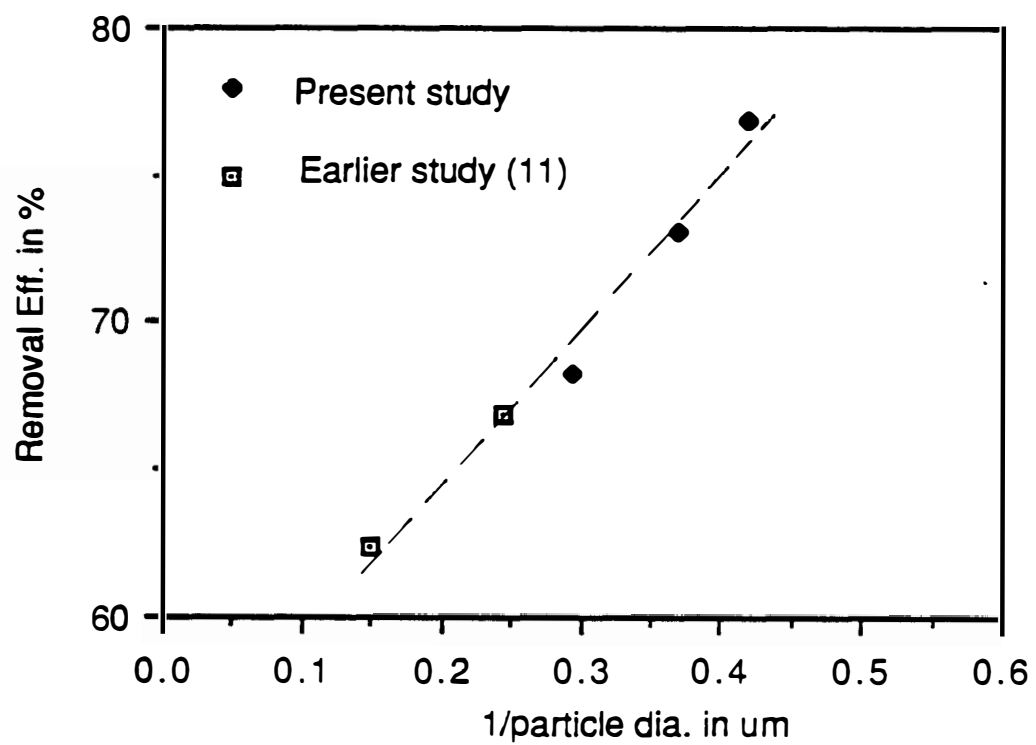


Figure 4-8. Inverse of particle diameter vs. removal efficiency.

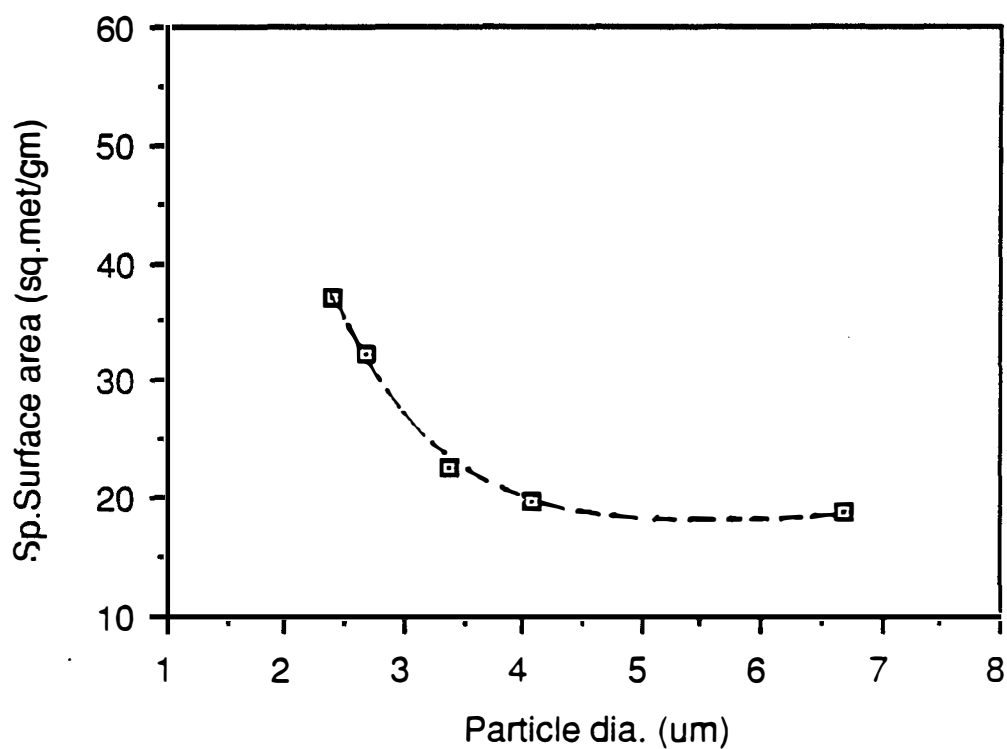


Figure 4-9. Specific surface area measured for different particle sizes.

values with spray dryer removal efficiencies obtained during pilot plant tests. Average values of removal efficiency attained at a stoichiometric ratio of around one, with sorbent particles of different sizes and specific surface areas are shown in Table 4-4. The results show a gradual increase in surface area with decrease in particle size. The improvements in spray dryer removal efficiency corresponds with the increases in specific surface area. Figure 4-10 depicts this trend. These tests reveal a strong influence of sorbent surface area on the spray dryer SO₂ removal efficiency. The trend of the curve is observed to be in close agreement with earlier research by Klingspor (46). The tendency of the curve with the data from this study, does not show any limitation on the maximum achievable efficiency. Information on such limitations is of paramount importance for the industrial applications. In the absence of further pilot data, a computer model simulated to these conditions can furnish such information. The tests in the present study indicate that enhancement in SO₂ removal efficiency across the spray dryer is possible by increasing the sorbent surface area, however there may be a limitation on the enhancement at points well below the theoretical utilization values. In the present study enhancement is obtained by grinding the slurry. As indicated earlier, the grinding operation was carried out for nearly 12 hours for a 55 gallon slurry to reduce the particle size from 3.4 microns to 2.4 microns. The tower mill in which grinding was done, operated on a 10 HP motor. These details can give an idea about the magnitude of the power requirements on an industrial scale.

In the literature, the sorbent performance is often explained by using several empirical models. Referring to Figures 4-3 through 4-5, the lines through the data and origin do not cross the perfect utilization line which shows that the pilot plant data do not contain any abnormalities. This provides an opportunity to check the data with empirical models. The efficiency data are checked against an empirical model by Bjerle et al. (62) . As per them, sorbent surface area can be linked empirically to the performance of the sorbent as under

Table 4-4. Average particle diameters and corresponding surface area and efficiency values at SR=1

d_p microns	SP.SURFACE AREA M ² /G	S.D REMOVAL EFF. %
2.4	37.10	76.9
2.7	32.17	73.1
3.4	22.65	68.3
4.1	19.83	66.9
6.7	18.93	62.4

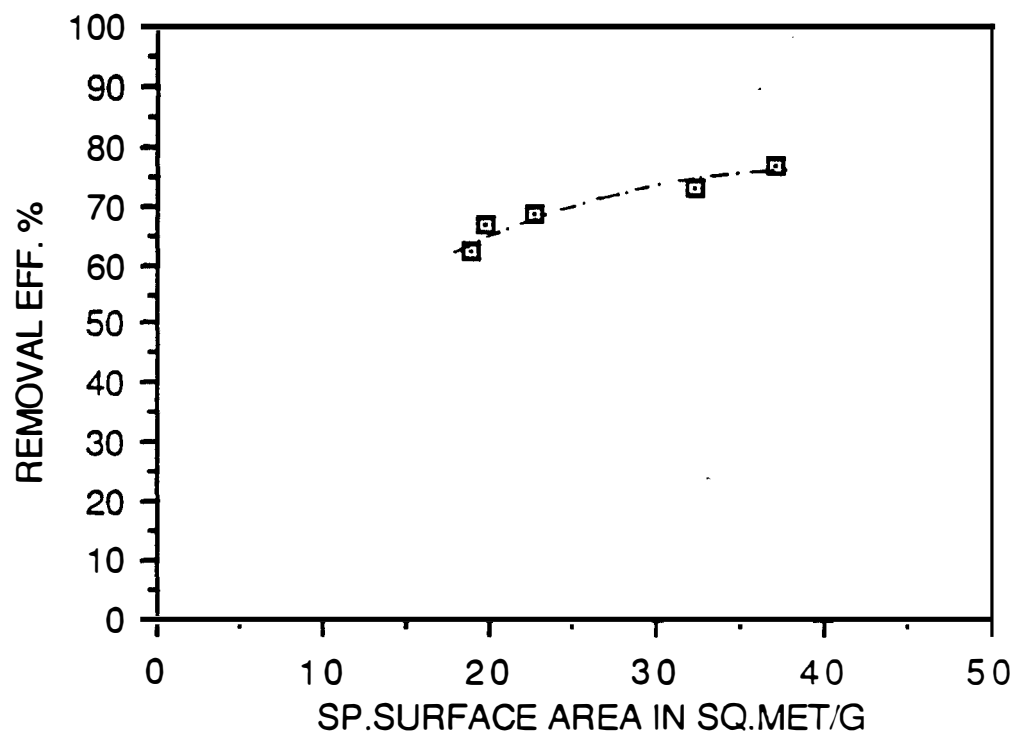


Figure 4-10. Specific surface area vs. removal efficiency.

$$-\ln (1-E) = K S_p SR t + B \quad (4-1)$$

where

E= Efficiency, fraction

K= Reaction rate constant, g/m² - sec.

S_p=Specific surface (B E T) area, m²/g

SR=Stoichiometric ratio

t=drying time

B=a constant

The above equation indicates that reaction rate increases exponentially with the B E T surface area, keeping other conditions constant. The validity of the model is checked by plotting the efficiency data (obtained at a stoichiometric ratio of one) as per the above equation. The data yielded a straight line as presented in Figure 4-11, showing the agreement with the model. The trend observed is found to be similar to the earlier work by Bjerle et al. (62). However, the tendency of efficiency limitation at higher surface area values is not observed in this model.

S E M micrographs of the three slurries tested at the pilot facilities showed relatively same crystal shape as expected. The micrograph for the 2.4 micron slurry is presented in Figure 4-12. The crystal morphology seem to be similar to the earlier micrograph (Fig. 4-2) for the regular lime slaked in laboratory.

C. INCORPORATION OF SURFACE AREA INTO MODEL:

To further investigate the aspects of particle size reduction and its effect on removal efficiency, a computer model is thought to be more appropriate to use, in the absence of pilot plant data. SPRAYMOD-M, a mechanistic model developed by Partridge (57) was chosen to look into the aspects of the present study. However, this model was not tested for different particles sizes, previously. In order to check its validity at different sorbent particle sizes, the

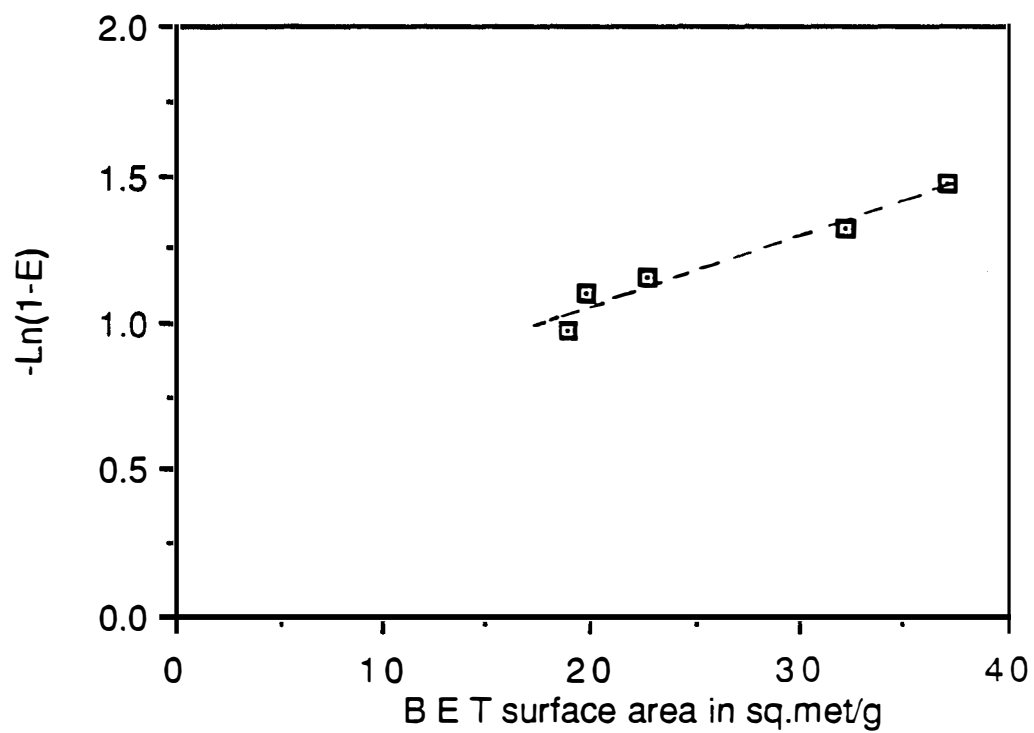


Figure 4-11. Surface area vs. negative log penetration.

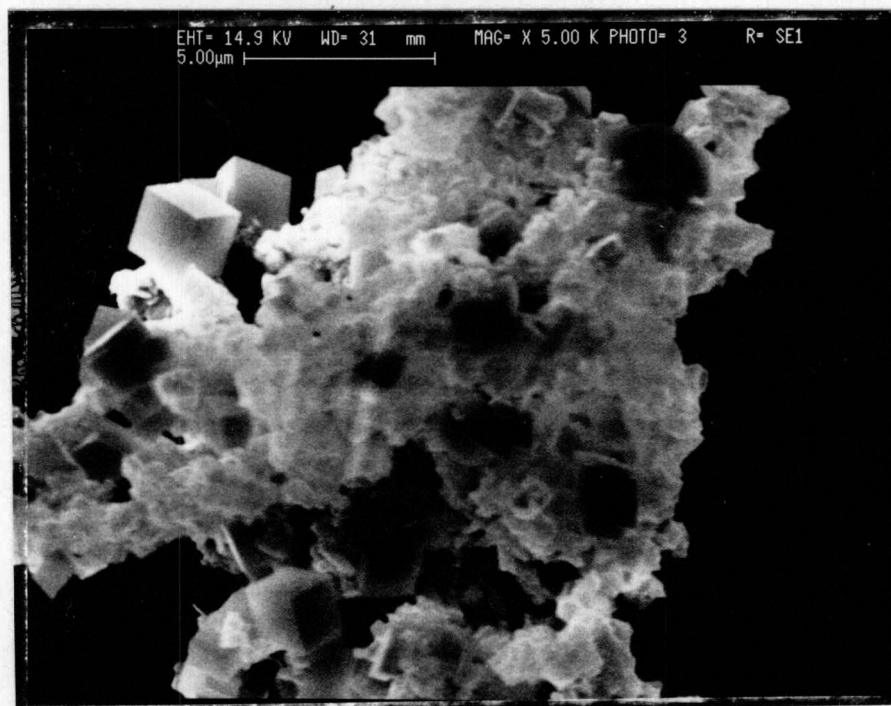


Figure 4-12. SEM micrograph for 2.4 micron slaked lime slurry.

model was run for those conditions and compared with the actual pilot plant data. The comparison is shown in Fig. 4-13. The model did not predict the tendency of the relationship between inverse of particle diameter and spray dryer removal efficiency, similar to the pilot plant data. It is to be noted that the model uses calculated values for sorbent surface areas, which are quite smaller than the measured values in the present study. In order to give an idea about the difference in magnitude, a comparison between calculated (for a spherical shape) surface areas and measured values is presented in Table 4-5. It is recognized that the model (SPRAYMOD-M), could be improved so that the predictions are much more closer to the actual data. The model modifications are approached as presented below.

The original 'SPRAYMOD' model by Damle (6) was modified by Partridge (57) for the constant rate period and was called 'SPRAYMOD-M'. This modified version used a comprehensive approach to account for the SO₂ absorption and reaction phenomena occurring during the constant rate period in a spray dryer. The model (SPRAYMOD-M) basically used heat transfer relations and overall methodology for computations from the original model. The modified model, however, introduced a mechanistic approach by considering all resistances involved in this mass transfer process and thereby following a rigorous calculation procedures, for the constant rate period.

Both the original model and modified version recognized that the resistance due to dissolution of Ca(OH)₂ particles was highly significant in calculating controlling mass transfer rates. The models calculated the rate of dissolution using film theory as under:

$$R_p = D_{\text{slaked lime-water}} (\pi d_p^2) ((C_l^* - C_l) / \delta) \quad (4-1A)$$

where

R_p = rate of dissolution for single Ca(OH)₂ particle

d_p = diameter of Ca(OH)₂ particle

$D_{\text{slaked lime-water}}$ = diffusivity of Ca(OH)₂ in water

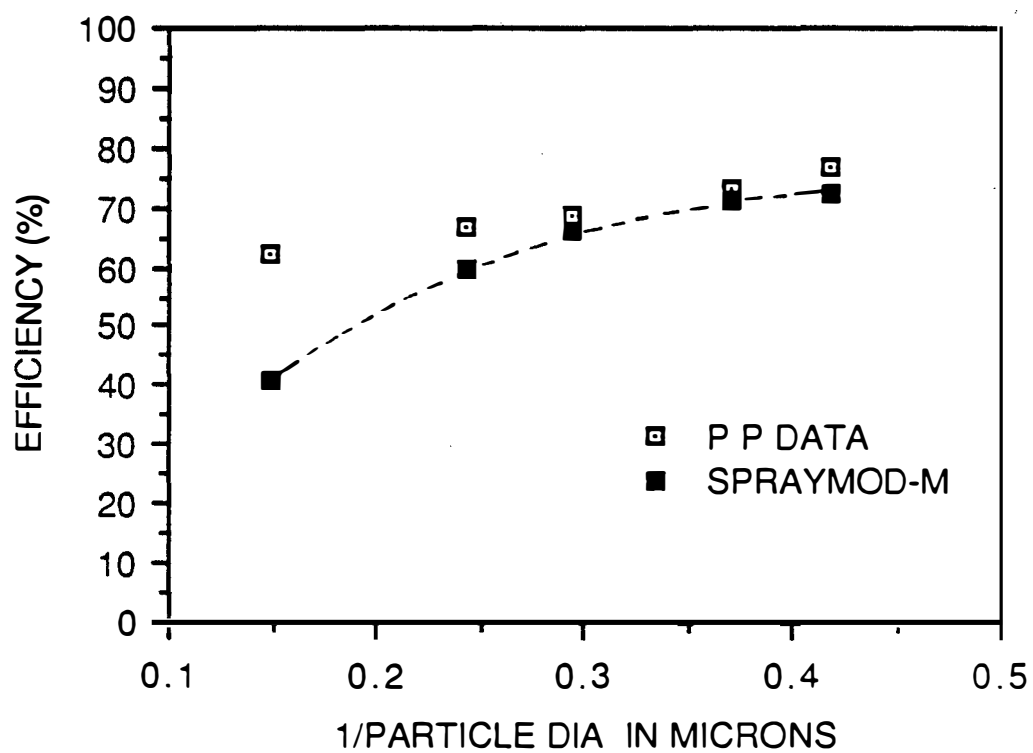


Figure 4-13. Comparison of pilot plant data with SPRAYMOD-M predictions.

Table 4-5. Comparison between calculated and measured values for the slaked lime specific surface areas.

Ca(OH) ₂ particle size um	Specific Surface area in M ² /G	
	calculated	measured
2.4	1.12	37.10
2.7	0.99	32.17
3.4	0.79	22.65
4.1	0.65	19.83
6.7	0.40	18.93

C_l^* = equilibrium solubility concentration

C_l = concentration of slaked lime in bulk solution

δ = film thickness responsible for slaked lime dissolution

The two models used different equations for calculating film thickness, however, both models considered the primary slaked lime particle as spherical in shape. In developing the combined rate equation in SPRAYMOD-M, the same approach was used. In calculating the rate of dissolution, surface area was represented by πd_p^2 as per the assumption of a spherical particle. As indicated earlier, slaking aspects of lime affect not only the particle size but also the surface area of the resulting slurry. Out of all shapes, spheres offer the smallest surface area per unit volume. By considering slaked lime particle to be represented by a spherical shape and thereby calculating the lowest possible surface area, the Ca(OH)_2 dissolution rate might be underestimated. The previous versions of the model calculate mass transfer rates based on slaked lime dissolution resistance and compare these with the rates due to other resistances and / or combined resistance to arrive at the control rate. Any underestimation in slaked lime dissolution rate can make this resistance the controlling resistance. In other words, a relatively accurate estimation can be made by inputting a realistic surface area of slaked lime particle into the model. The above discussion suggests that slaked lime dissolution rate can be better represented by considering a measured surface area rather than a calculated area of an assumed shape. This may eliminate a possible assumption error.

The present work involved testing of various slurries with different surface areas for their performance in the spray dryer. In order to apply SPRAYMOD-M for these slurries and to test the other data collected previously at the pilot facilities, the model (SPRAYMOD-M) is further modified. The new version (referred to here in as SPRAYMOD-N) calculates the mass transfer rates based on measured sorbent specific surface area (as M^2/G). The combined

rate equation is re-derived to accommodate the new measured variable i.e specific surface area. The computer program with these modifications is presented in Appendix-A.

As all the features of SPRAYMOD-M have been kept intact in the present model, a brief description of this model is presented below. SPRAYMOD-M was based on film theory for an instantaneous liquid phase reaction where gas species, and the solid species dissolved into a liquid medium, react. A single rate relationship was developed for the constant rate period, combining individual resistances for the gas phase mass transfer, liquid phase mass transfer and sorbent dissolution. Film theory was applied to predict mass transfer coefficients for the liquid phase and solid dissolution. The gas phase mass transfer coefficient was obtained from heat and mass transfer analogies. SPRAYMOD-M calculated the molar rates based on gas phase resistance, slaked lime dissolution resistance and a combined resistance equation. These rates were compared and the smallest molar rate was chosen to be the control rate for the time increment considered. Simultaneous heat transfer calculations were performed for the evaporating droplet considering the same time increment to arrive at the moisture content. Constant rate period of the wet particle stage was assumed to cease at the critical moisture content of the droplet. Physical properties of both gas and liquid phases were predicted using various relationships. Molar density of gas phase, saturation solubility of Ca(OH)_2 and diffusivity of SO_2 in flue gas were determined as per Damle (6). Equations for calculating liquid phase diffusivities for SO_2 and Ca(OH)_2 were developed using the procedures adopted by Pearson (54) and Sada (53). Liquid film thickness was calculated using film theory and by setting some limits (minimum and maximum). The minimum possible thickness for liquid film during solid dissolution was chosen to be equal to one-half of the particle diameter. Partridge (57) presented all the detailed expressions for the above calculations.

The new version, SPRAYMOD-N, seeks input through two data files. The first data file contents are similar to those used in SPRAYMOD-M version. This consists of data about inlet gas conditions, operating parameters and sorbent properties. Gas conditions data include inlet SO₂ concentration, inlet gas temperature, flue gas molecular weight and inlet water content of the flue gas. The operating conditions include, approach to adiabatic saturation temperature, stoichiometric ratio, residence time of gas phase and type of mixing conditions in the spray dryer. In the present work, plug flow conditions are selected to represent the mixing in spray dryer as it is reported that the model responded well in this mode (57). Sorbent data include inlet droplet diameter and its temperature, sorbent particle diameter, density and molecular weight of sorbent, critical and equilibrium moisture contents. The model requires a value for dry sorbent reaction rate coefficient to extend the run into dry particle stage. As the present version attempts to model only the constant rate period of the wet particle stage, this coefficient value is supplied as equal to zero. Typical parameter values that are supplied as input for the program simulation are presented in Figure 4-14. The second data file furnishes the specific surface area (in M²/G) values for each set of test conditions. In other words, if more than one test condition is simulated involving two different slaked limes or slaked limes with the same specific area, the variable data have to be supplied for each case. The model reads the specific surface area value in M²/G for each case and displays that value on the screen until the entire simulation is completed for that case. The supplied specific surface area value units are changed in the program to be compatible with the other variable units.

The previous version (SPRAYMOD-M) was written in such a way that, for each set of test conditions, two computer programs had to be executed separately to obtain the final output. In the new version, the actual simulation program and the 'output read' program are compiled (using IBM basic compiler) and combined together. The program at its present form, requires the user input for the number of data set points and the name of the first input data

Inlet Gas Conditions -

Inlet Gas Temperature - 148.89 C
% Water in Inlet Gas - 6 %
Inlet SO₂ Concentration - 1000 ppm
Molecular Weight of Dry Inlet gas - 29.4

Operating Parameters -

Approach to Saturation - 11.1 C
Stoichiometric Molar Ratio - 1
Mass Fraction of Sorbent in Fresh Solids - 1
Recycle Solids Ratio by Mass - 0
Mass Fraction of Sorbent in Recycle - 0
Residence Time of Gas Phase - 17 sec
Flow System in Spray Dryer - Plug Flow

Sorbent Properties -

Inlet Droplet Diameter - 79.99999 um
Inlet Droplet Temperature - 35 C
Form of Sorbent - Slurry
Sorbent Particle Diameter - 3.4 um
Molecular Weight of Sorbent - 74.1
Density of Solid Sorbent - 2.24 gm/cm³
Critical Moisture Content - 29.2%
Equilibrium Moisture Content - 6%
Dry Sorbent Reaction Rate Coefficient - 0 cm³/gmole/sec
Assumed Spray Dryer Efficiency - 50%

Program Parameters -

Maximum Allowable Time Step - .1 sec
Time between Printouts - .5 sec
Time Step Control Parameter - .01

Figure 4-14. Typical input parameters for SPRAYMOD-N.

file, at the beginning of the simulation. As soon as the simulation is completed for all the data set points, the program invokes the printer and all the output is printed onto a hard copy. This improvement is found to be more convenient and quicker when handling larger number of data sets.

The derivation for obtaining the new combined rate equation involving surface area is presented below:

Referring to Figure 2-2 (on page 29) the rate equations applicable for each resistance can be given by

$$-r_A = K_g (\pi d_d^2) (C X_{g,A} - C X_{d,A}) \quad (4-2)$$

$$-r_A = K_{AL} (\pi d_d^2) (C_{Ai} - 0) (X_0/X) \quad (4-3)$$

$$-r_A = K_{BL} (\pi d_d^2) (C_B - 0) ((X_0)/(X_0 - X)) \quad (4-4)$$

$$-r_A = K_s (SA) (C_s - C_B) \quad (4-5)$$

where

$-r_A$ = SO₂ removal rate during constant rate period (gmole/s)

K_g = gas side mass transfer coefficient (cm/s)

d_d = droplet diameter (cm)

C = molar density of the gas phase (gmole/cc)

K_{AL} = liquid side mass transfer coefficient for SO₂ (cm/s)

K_{BL} = liquid side mass transfer coefficient for Ca(OH)₂ (cm/s)

K_s = mass transfer coefficient for solid dissolution (cm/s)

SA = total surface area for slaked lime particles in a droplet (cm²)

$X_{g,A}$ = mole fraction of SO₂ in gas phase

$X_{d,A}$ = mole fraction of SO₂ at the droplet surface

C_{Ai} = concentration of SO₂ at the gas-liquid interface (gmole/cc)

C_B = concentration of Ca(OH)₂ in the bulk liquid (gmole/cc)

C_S = saturation solubility of Ca(OH)_2 in the liquid phase (gmole/cc)

X = distance from gas-liquid interface to reaction zone (cm)

X_0 = liquid film thickness (cm)

Also $K_S = D_{BL} / \partial R_L$ from film theory (4-6)

$C X_{d,A} = H_A C_{Ai}$ from Henry's law (4-7)

$(K_{AL} / K_{BL}) = ((D_{AL}/X_0) / (D_{BL}/X_0)) = D_{AL}/D_{BL}$ as per
Levenspiel (48) (4-8)

where

D_{AL} = liquid phase diffusivity for SO_2 (cm^2/s)

D_{BL} = liquid phase diffusivity for Ca(OH)_2 (cm^2/s)

H_A = Henry's law constant for SO_2

∂ = film thickness for solid dissolution (cm)

R_L = lime fraction remaining

From eq. (4-5)

$$(C_S - C_B) = \frac{-r_A}{K_S SA}$$

Using eq. (4-6)

$$(C_S - C_B) = \frac{-r_A \partial R_L}{D_{BL} SA}$$

or $C_B = C_S + \frac{r_A \partial R_L}{D_{BL} SA}$ (4-9)

From eq. (4-2)

$$\frac{-r_A}{K_g \pi d^2} = C X_{g,A} - C X_{d,A}$$

or $C X_{d,A} = C X_{g,A} + \frac{r_A}{K_g \pi d^2}$ (4-10)

From eq. (4-3)

$$X = \frac{-K_{AL} \pi d_d^2 C_{Ai} X_0}{r_A} \quad (4-11)$$

Using eq. (4-8)

$$X = \frac{-D_{AL} \pi d_d^2 C_{Ai}}{r_A} \quad (4-12)$$

From eq. (4-8) and (4-12)

$$X_0 - X = \frac{D_{BL}}{K_{BL}} + \frac{D_{AL} C_{Ai} \pi d_d^2}{r_A} \quad (4-13)$$

Using eq. (4-8) and (4-13) into eq. (4-4)

$$-r_A = \frac{K_{BL} \pi d_d^2 C_B (D_{BL} / K_{BL})}{(D_{BL} / K_{BL}) + (D_{AL} C_{Ai} \pi d_d^2 / r_A)}$$

By rearranging

$$-r_A (D_{BL} / K_{BL}) - D_{AL} C_{Ai} \pi d_d^2 = \pi d_d^2 C_B D_{BL} \quad (4-14)$$

Combining eq.(4-7) and (4-10)

$$C_{Ai} = \frac{C_{Xg,A}}{H_A} + \frac{r_A}{K_g \pi d_d^2 H_A} \quad (4-15)$$

Substituting C_B value from eq.(4-9) and C_{Ai} value from eq.(4-15) into eq.(4-14)

L.H.S of eq.(4-14) will be

$$= -r_A (D_{BL} / K_{BL}) - \frac{C_{Xg,A} D_{AL} \pi d_d^2}{H_A} - \frac{r_A D_{AL} \pi d_d^2}{K_g d_d^2 H_A}$$

and R.H.S of eq.(4-14) will be

$$\begin{aligned} &= (C_S + \frac{r_A \partial R_L}{D_{BL} SA}) D_{BL} \pi d_d^2 \\ &= C_S D_{BL} \pi d_d^2 + \frac{r_A \partial R_L \pi d_d^2}{SA} \end{aligned}$$

Rearranging the terms of r_A in the above

$$-r_A ((D_{BL}/K_{BL}) + (D_{AL}/K_g H_A) + (\partial R_L \pi d_d^2 / SA)) \\ = \pi d_d^2 ((D_{AL} C_{X_{g,A}} / H_A) + D_{BL} C_s)$$

Dividing through out by D_{AL}

$$-r_A ((D_{BL}/D_{AL}) (1/K_{BL}) + 1/(K_g H_A) + (\partial R_L \pi d_d^2 / SA D_{AL})) \\ = \pi d_d^2 ((C_{X_{g,A}} / H_A) + (D_{BL}/D_{AL}) C_s)$$

Using eq.(4-8) (for $(D_{BL}/D_{AL} = (K_{BL}/K_{AL})$ relation) in the above equation

$$-r_A ((1/K_{AL}) + (1/(K_g H_A)) + (\partial R_L \pi d_d^2 / (SA D_{AL}))) \\ = \pi d_d^2 ((C_{X_{g,A}} / H_A) + (D_{BL}/D_{AL}) C_s)$$

or

$$-r_A = \frac{\pi d_d^2 ((C_{X_{g,A}} / H_A) + (D_{BL}/D_{AL}) C_s)}{((1/K_{AL}) + (1/(K_g H_A)) + (\partial R_L \pi d_d^2 / (SA D_{AL})))} \quad (4.16)$$

The above equation is used in the modified model to calculate the rate due to combined resistances. The model still requires particle diameter as input, to calculate the film thickness.

D. COMPARISON OF SPRAYMOD-N WITH PILOT PLANT DATA:

Actual pilot plant conditions were simulated with the two versions of the model. The comparison between the model predictions and actual pilot plant data for inlet SO_2 concentration of 1000 ppm, stoichiometric ratio of one and approach to saturation temperature of 20° F, is presented in Figure 4-15. SPRAYMOD-N predictions are found to be a little higher than the actual pilot plant data at larger particle sizes, however the trend of the data predicted, which is a straight line, agrees well with the actual data. This straight line trend also agrees with the earlier research by Norman (14). This suggests that by incorporating measured surface area into the model, more realistic predictions can be made.

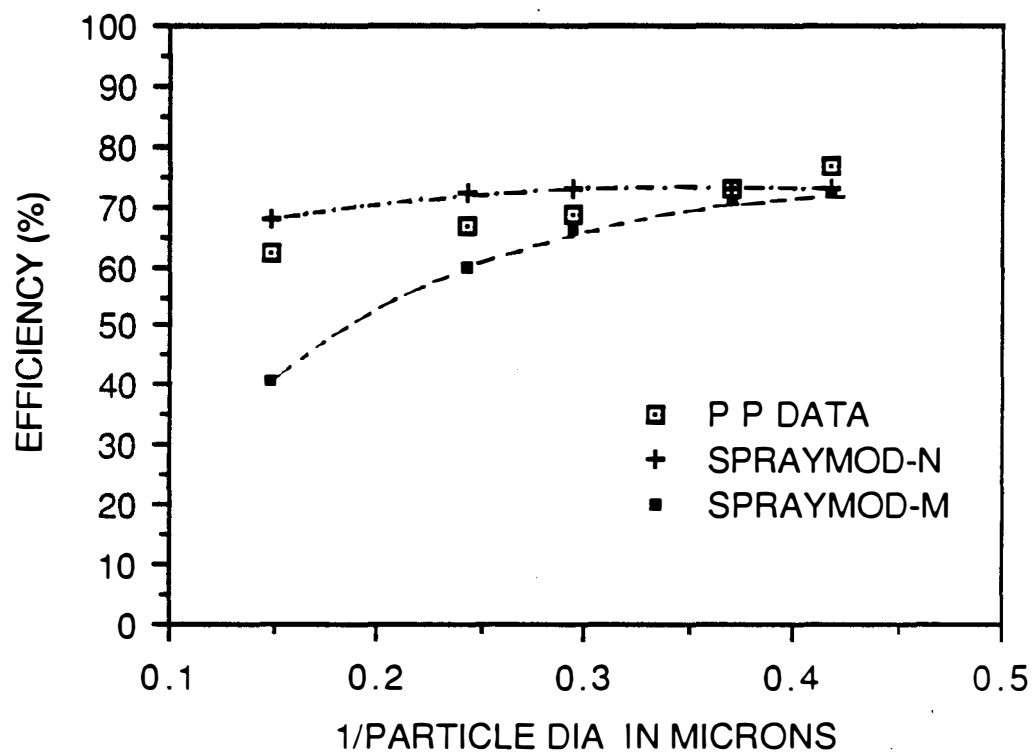


Figure 4-15. Comparison of predictions from SPRAYMOD-N and SPRAYMOD-M versions.

As the new version is observed to be predicting well, it is checked against all the pilot plant data obtained in this study. The efficiency values obtained from this model are compared with the values from various tests conducted at the pilot facilities. Figure 4-16 shows such comparison for the 2.4 micron slaked lime slurry at an inlet SO₂ concentration of 1000 ppm and a 20° F approach to saturation temperature. The model predictions are very close to the actual values. There is some under prediction from the model, however it is to be noted that model uses only the constant rate period for the predictions. Similar comparisons of the performance data for 2.7 micron and 3.4 micron slaked limes are presented in Figures 4-17 and 4-18 respectively. In order to assess the spread of the predicted data, the residuals (predicted value - actual pilot plant value) of predictions are plotted against the actual pilot plant efficiency data, as shown in Fig. 4-19. The plot shows that the model predictions are more or less very close to the actual pilot plant values in low efficiency range, but there is under prediction at higher SR values. The model predictions are reasonably good in overall. It is interesting to note that the model predicts a near 100 percent lime utilization up to a stoichiometric ratio of around 0.6 for all slaked limes, which is similar to the actual observations at the pilot facility, in general. In order to check the sensitivity of the model on specific surface area, the model was run at different surface area values, while keeping the diameter of the particle same. When the model was run for 3.4 um particles, with surface areas of 5, 10, 20 and 25 M²/G, the difference in predicted efficiencies between the first case and the last case was less than one percent. It shows that the new version of the model is not sensitive to specific surface area, as much as the particle diameter. It is to be noted that the particle diameter is used in SPRAYMOD-M to calculate the liquid film thickness around the Ca(OH)₂ particle, and SPRAYMOD-N uses the same calculations. This suggests that liquid film thickness calculations are dominating the surface area variable, and much more sensitive to the model predictions, than anticipated.

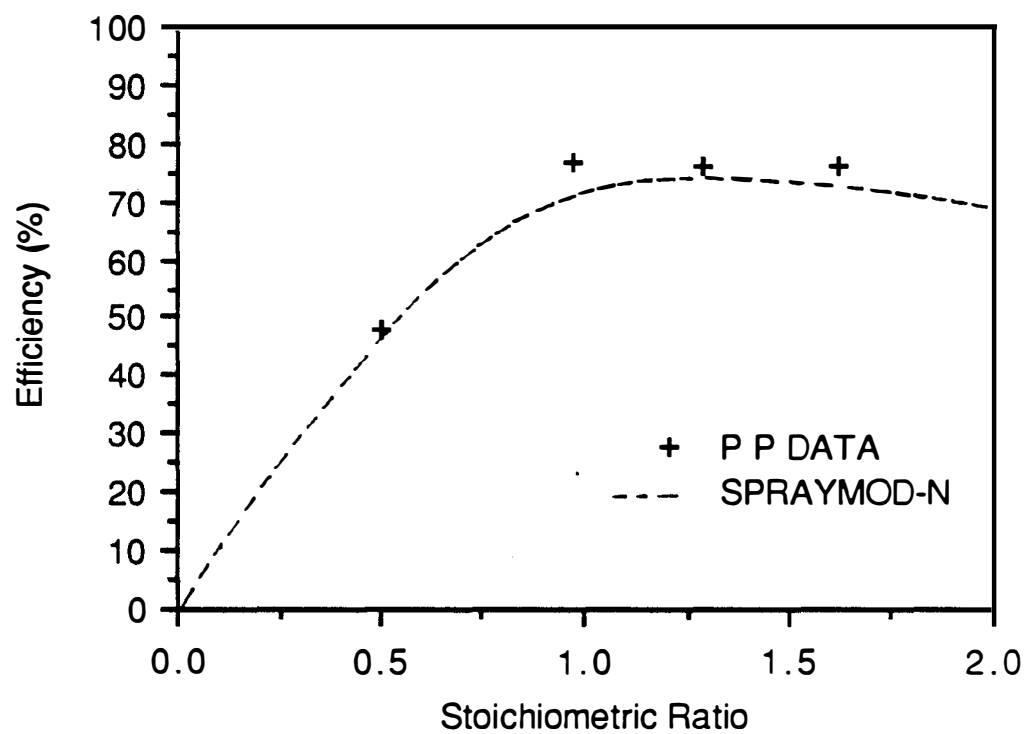


Figure 4-16. Comparison of pilot plant data with SPRAYMOD-N predictions for 2.4 micron slaked lime.

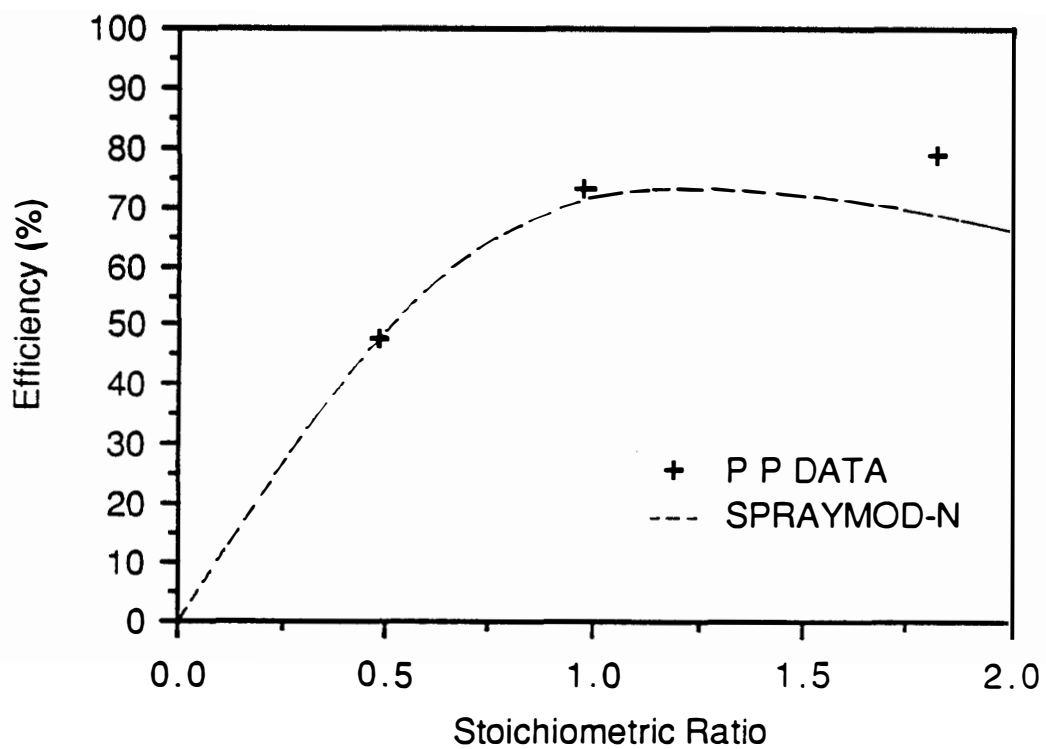


Figure 4-17. Comparison of pilot plant data with SPRAYMOD-N predictions for 2.7 micron slaked lime.

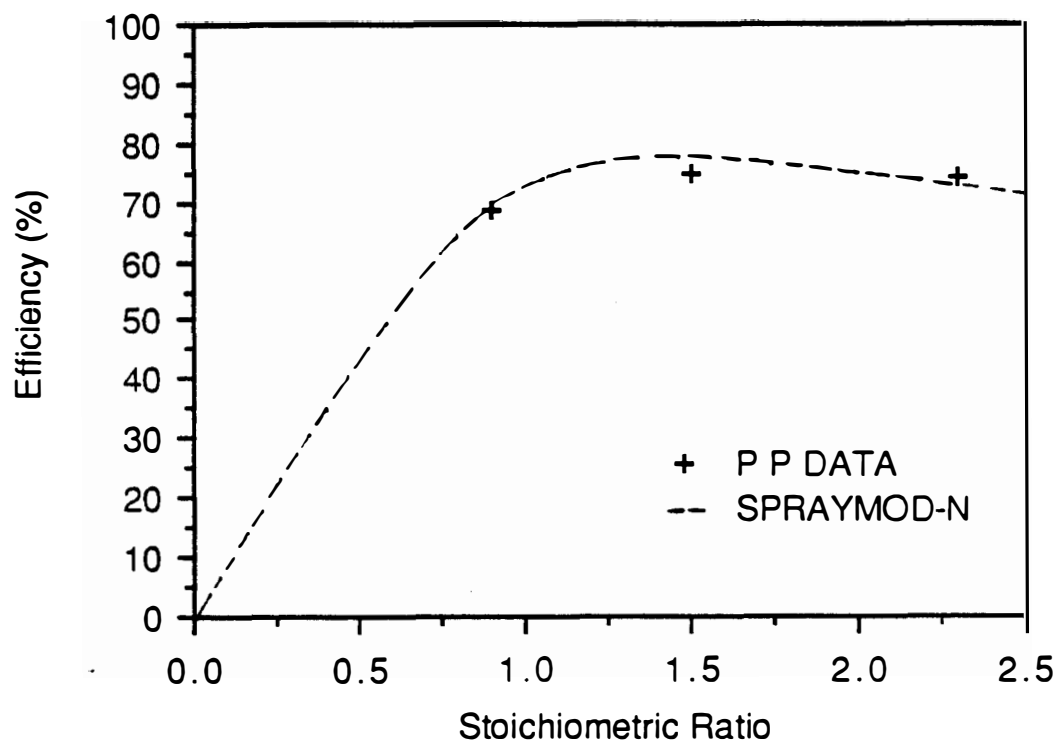


Figure 4-18. Comparison of pilot plant data with SPRAYMOD-N predictions for regular slaked lime.

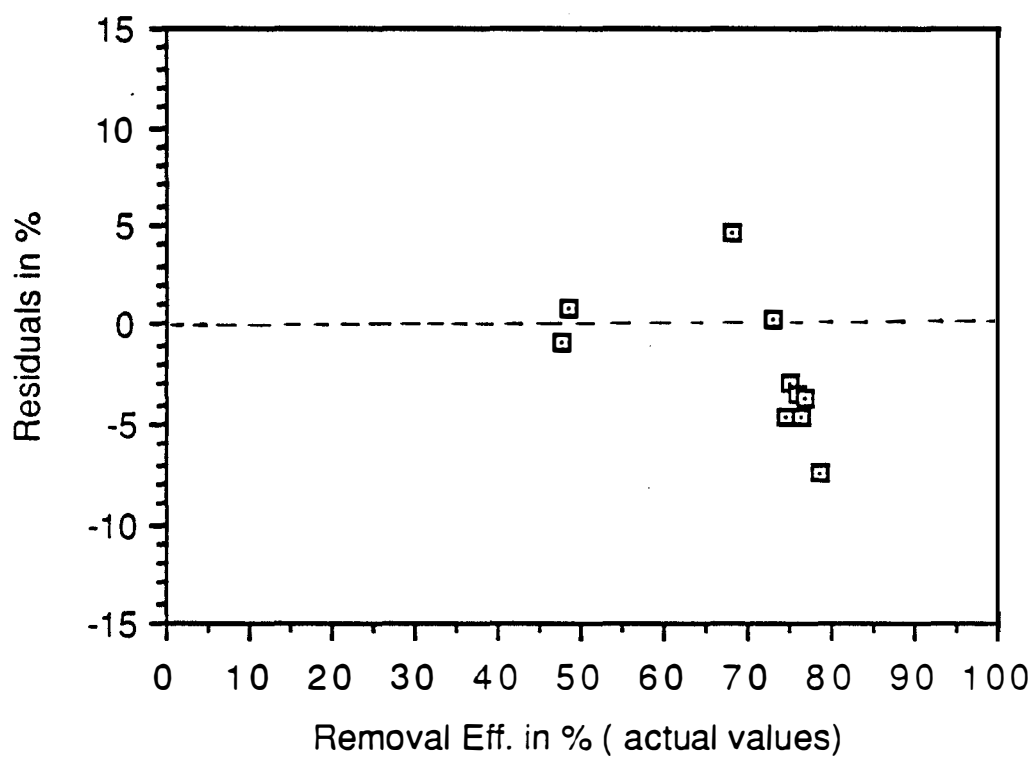


Figure 4-19. Residuals of prediction vs. pilot plant efficiency data

Realizing that SPRAYMOD-N is predicting reasonably well for the pilot plant data in the present work, it is thought that the model could be used to predict the maximum possible efficiency at the test conditions. In the spray dryer system involving slaked lime slurry, the rate limiting step is dependent upon the reactivity of the slaked lime and / or calcium - to- sulfur ratio. As per Klingspor (46) a system controlled by the dissolution rate is likely to prevail at Ca / S ratios below or close to unity with a low to normal reactivity sorbent. As the SR increases, more and more of the removal period will be controlled by gas-film resistance. It is evident that a gas-film controlled system should give the maximum possible efficiency (during constant rate period), because in this system, mass transfer rates with liquid film resistance and slaked lime dissolution resistances are higher than the rate with gas film resistance. In other words, in this situation, there will be enough Ca(OH)_2 available to react and the liquid film will have enough capacity to absorb whatever SO_2 that passes through the gas film. This puts the system in an ideal condition in which everything else on the other side of gas film is ready to react with what ever SO_2 that can pass through the gas film. If these conditions are obtained at a stoichiometric ratio of one, the only resistance that can prevent from achieving 100 percent sorbent utilization, would be the gas film resistance. The situation during dry particle stage however, is quite different. During this stage, the mass transport takes place only through void volumes and interstices between elementary particles. Diffusion resistance through the product layer increases and dominates as time elapses. It is to be noted that the previous discussion about the gas film controlled system is applicable only for the period before the dry particle stage. As per Klingspor (46) a system in which the gas film controlled system dominates the overall removal period, can be obtained by substantially increasing the Ca / S ratio or by increasing the reactivity of the sorbent, i.e the surface area. It is to be noted that even though the sorbent Ca(OH)_2 can be processed to provide very high surface area,

achieving 100 percent or near stoichiometric lime utilizations depends upon the magnitude of gas film resistance and related mass transfer rate.

In the present work SPRAYMOD-N was run, specifically to consider gas film resistance alone and ignoring the other resistances, to obtain a maximum removal efficiency. This gas phase controlled system at the conditions of inlet SO₂ concentration 1000 ppm, approach to saturation temperature of 20⁰ F and SR of one, gave a removal efficiency value of 73.25. In order to run the model at smaller particle sizes, the corresponding surface areas are also required. As the measurements in this study are involved only up to particle sizes of 2.4 microns, developing a linear equation (by regression) relating inverse of particle size and specific surface area, is thought to be a reasonable approach. When linear regression is applied for all the five data points (for which surface area measurements are made in this study), as shown in Fig. 4-20, the following equation is obtained with a regression coefficient of 0.93.

$$\text{Sp.Surface area in m}^2/\text{g} = 5.0689 + 71.4758 (1/\text{particle dia. in } \mu\text{m}) \quad (4-17)$$

As the regression coefficient obtained is relatively low, another attempt is made without the data for 6.7 micron particles. The regression resulted a coefficient of 0.99, as shown in Fig. 4-21. The resulting equation is

$$\text{Sp.Surface area in m}^2/\text{g} = -6.4825 + 103.9471 (1/\text{particle dia. in } \mu\text{m}) \quad (4-18)$$

As the above equations are proposed to be used for smaller particle sizes (i.e higher 1/dp values), it is assumed that eq. 4-18, with a larger regression coefficient would be more appropriate to use. It is to be noted that the differences between the surface area values obtained from the above two equations, are not significantly high.

The model was run again in the regular mode (with all resistances) for different particle sizes, (with specific surface areas calculated as per eq. 4-18) the other conditions remaining the same as of earlier run. Figure 4-22 depicts the trend of increase in efficiency with

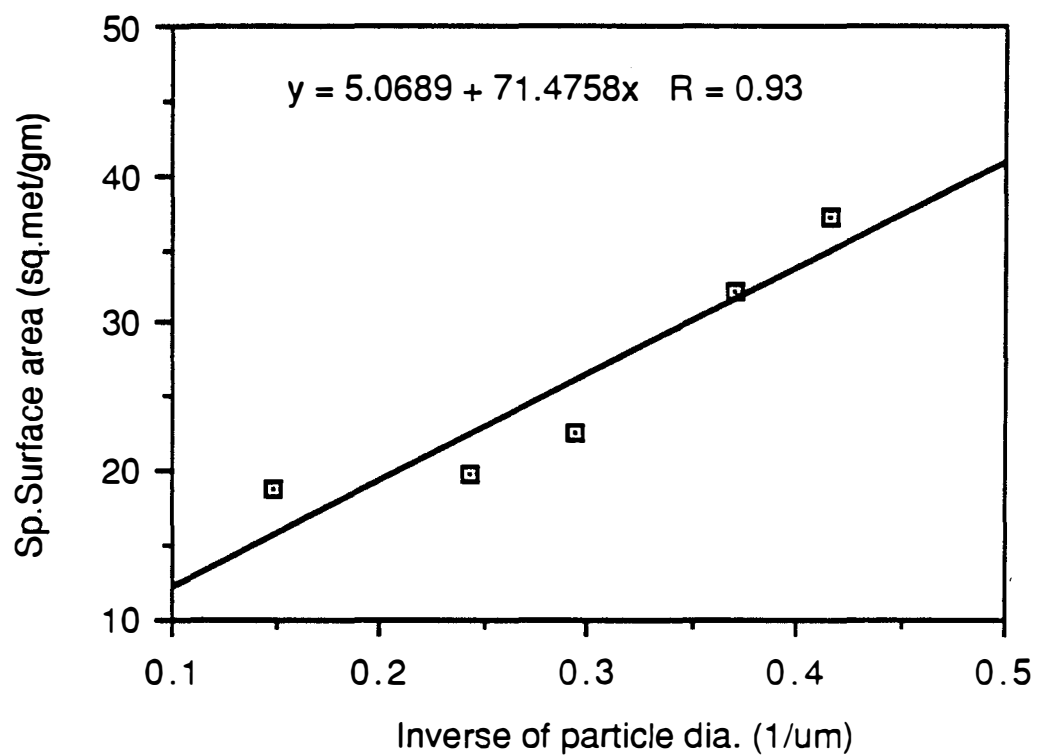


Figure 4-20. Linear Regression I, for specific surface area and inverse of particle size.

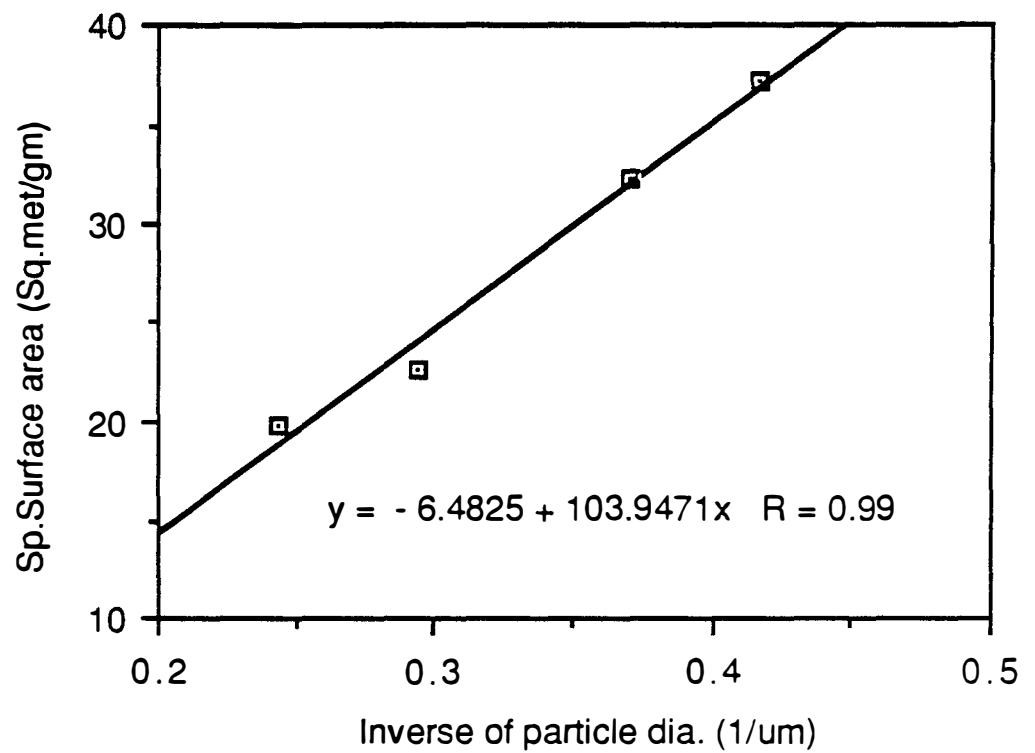


Figure 4-21. Linear Regression II, for specific surface area and inverse of particle size.

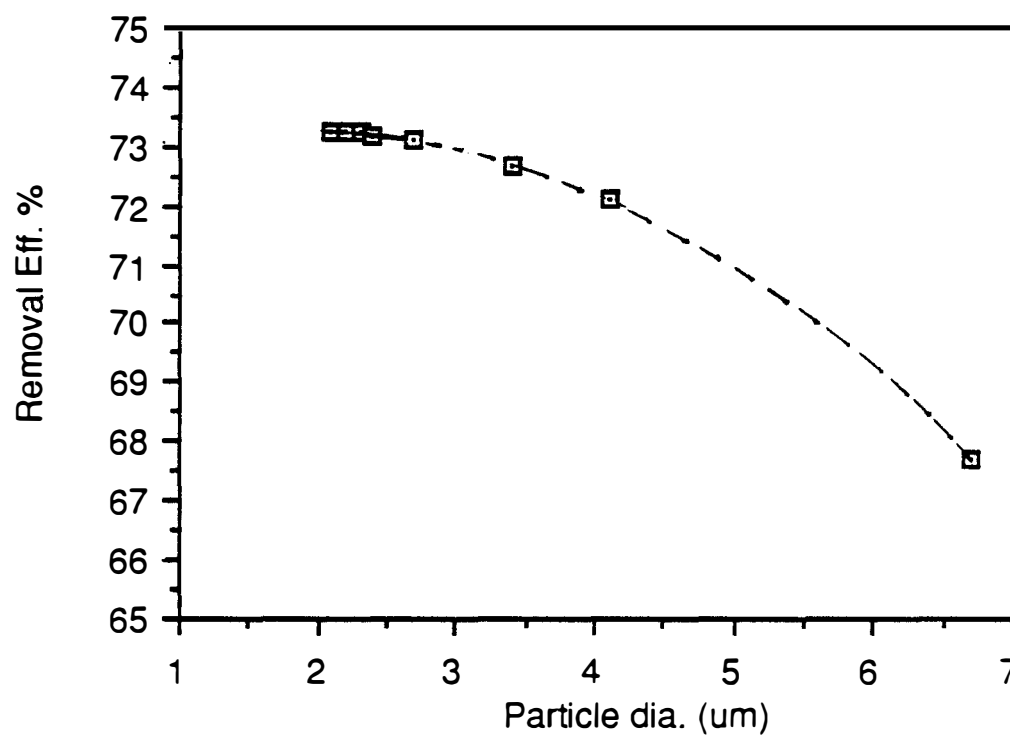


Figure 4-22. SPRAYMOD-N prediction for optimum particle size.

decrease in particle size. The efficiency curve gets flat at a particle diameter of 2.3 microns after achieving 73.25 percent removal. Any further decrease in particle size does not result in any improvements in the removal efficiency. In other words, as per the model a gas phase controlled system could be achieved with sorbent particles of 2.3 microns. However, it is to be noted that SPRAYMOD-N models only the constant rate period of the process and so the overall spray dryer efficiency values would be somewhat higher. The pilot plant tests in the present work gave an efficiency of 77 percent with 2.4 micron particles. This suggests that a gas phase controlled system might have been obtained or at least the system might have been very close to achieving those conditions. As SPRAYMOD-N predictions are closer to the actual pilot plant data, the above conclusion may be reasonably good. Further efforts were made to check into the gas side mass transfer coefficient estimation method used by the model. The model used eq. 2-18 to calculate the gas side mass transfer coefficient, which was obtained by following standard heat and mass transfer analogies. As such there is very little possibility that equation is totally incorrect. In order to check the magnitude of gas side mass transfer coefficient required to achieve 100 percent removal in a gas phase controlled system, SPRAYMOD-N was run with coefficient values quite higher than calculated values. The model in a gas phase control mode, gave a near 100 percent efficiency with a coefficient four times the value usually calculated. This indicates that in a normal mode, the equations should be under estimating by 300 percent. There is very little possibility for this to occur. This approach was also checked for normal runs. The model predicted 96 percent efficiency with gas side mass transfer coefficient four times the regular value, for a normal lime slurry with 3.4 micron particle size at a stoichiometric ratio of one. As per the experiences at the pilot plant, this value is impossible to achieve, which leads to the conclusion that gas side mass transfer coefficient calculations are at least reasonable. With this approach, it is concluded that gas phase

conditions might have been achieved in the pilot plant tests with the 2.4 micron slaked lime slurry.

Previous pilot plant test data accumulated over a period of time were also compared with the predictions from the new version of the model developed in this study. Eleven different data sets were involved. The exact details of the data generated at the pilot facilities can be found in an earlier work by Partridge (57). Operating conditions to simulate the model were chosen such that they represent average conditions of the data set. The summary of these conditions is presented Table 4-6. Performance of the model was analyzed by comparing the measured efficiency values at different stoichiometric ratios with predicted efficiency curve with some chosen stoichiometric ratios. The specific surface area value was considered to be equal to the measured value in this study for slaked lime without any grinding. Table 4-7 presents the important parameters of pilot plant data sets and corresponding figures in which comparisons with the model predictions are made. The comparison in Figure 4-23 through Figure 4-31 shows that model predictions are reasonably good. It is observed that the model predictions fall off at higher SR values. As mentioned earlier, the model considers only the constant rate period, which suggests that the fall off may be due to the absence of the falling rate period in the model. This indicates that the falling rate period becomes more significant at higher SR values. In general SPRAYMOD-N tended to under predict at higher stoichiometric ratios, however as indicated earlier, the predictions of 100 percent lime utilization up to SR's of around 0.6 are found to be in close agreement with day to day operations at the pilot plant. Comparing with the previous version of the model (SPRAYMOD-M) predictions, the present model values are found to be higher in general. These higher values may be attributed to the increased dissolution rates due to the incorporation of actual surface areas into the rate equation. As SPRAYMOD-M under predicted most of the data sets, the increased predicted values in the present work, closed

[illegible]

Table 4-7. Summary of important parameters of pilot plant data sets and figures showing the comparison between predictions and actual data.

DATA SET	FIGURE	SO ₂ CONC. ppm	TEMP. °F	APPROACH TEMP. °F
2	4-23	936-1222	302	16-18
3	4-23	940-1205	298	20
4	4-24	941-1074	342	35
5	4-25	1504-1620	293	31
6	4-26	2216-2416	259	15
7	4-27	2044-2353	295	15
8	4-28	1903-2149	279	25
9	4-29	1723-2184	266	35
10	4-30	2052-2146	309	35
11	4-31	1890-2057	340	35
12	4-31	2633-3178	336	35

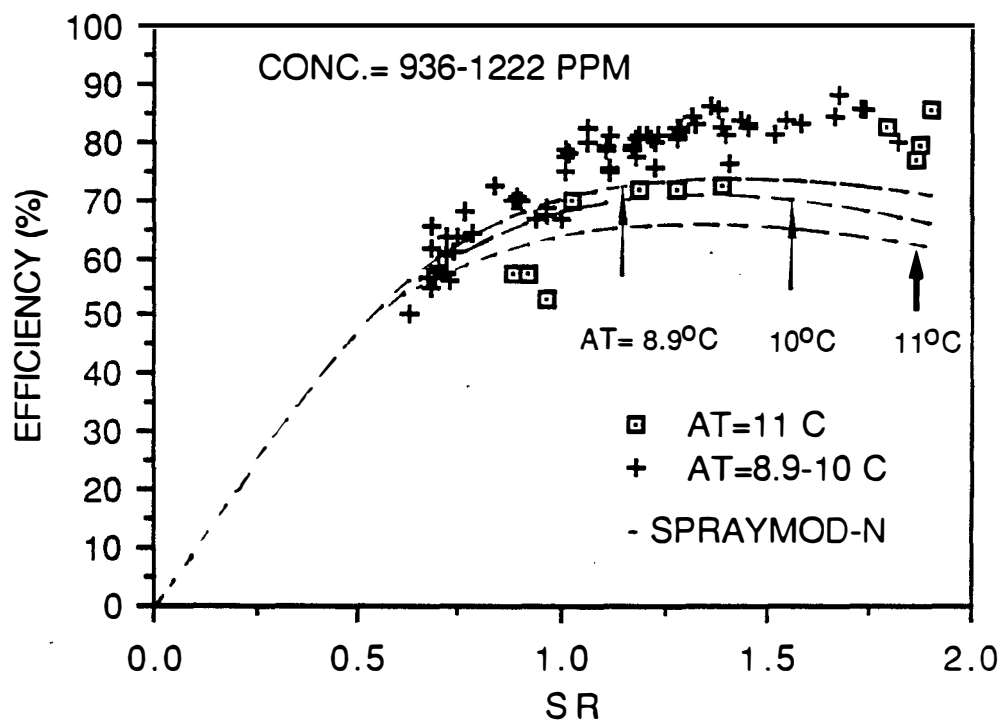


Figure 4-23. Comparison of SPRAYMOD-N predictions with actual pilot plant data for data sets 2 and 3.

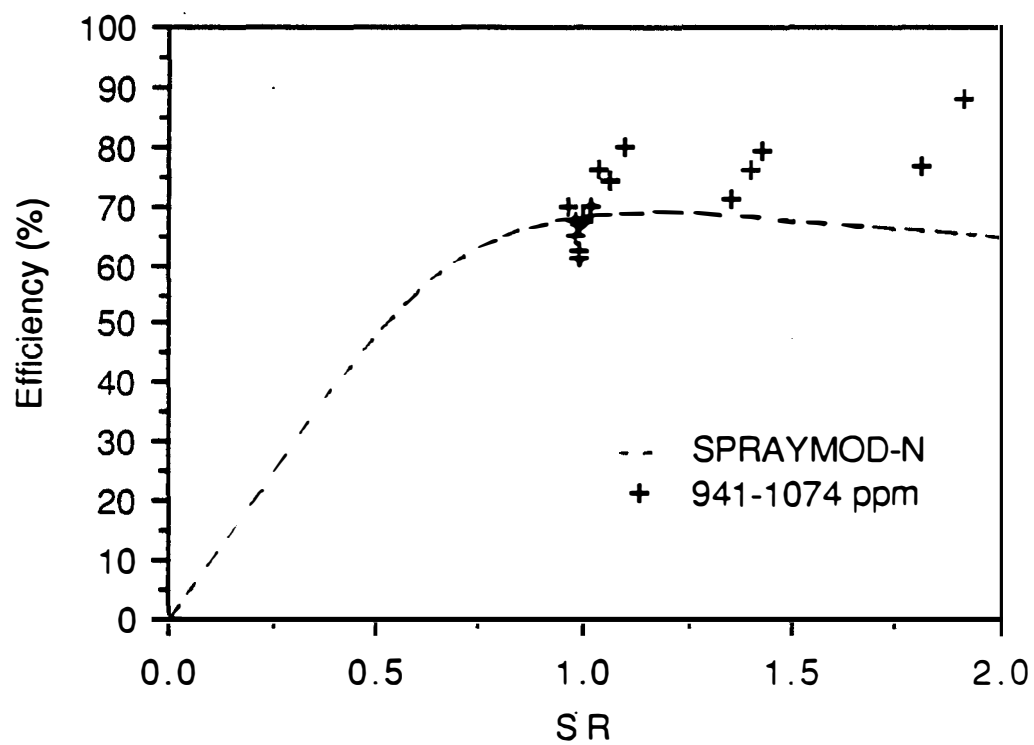


Figure 4-24. Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 4.

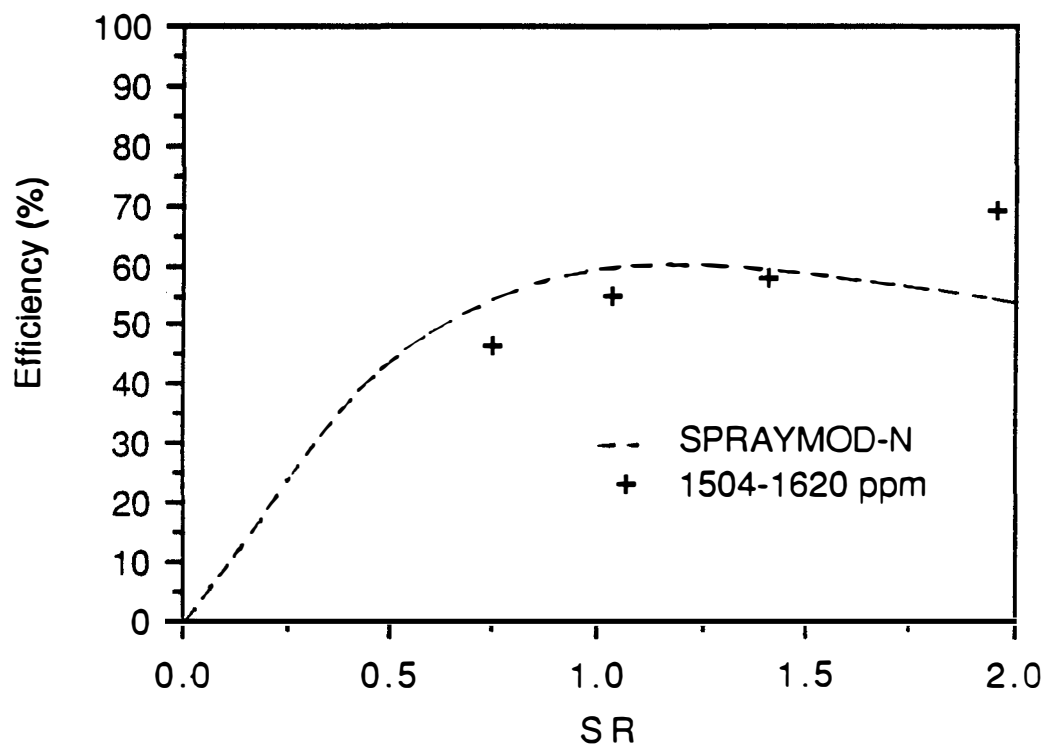


Figure 4-25. Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 5.

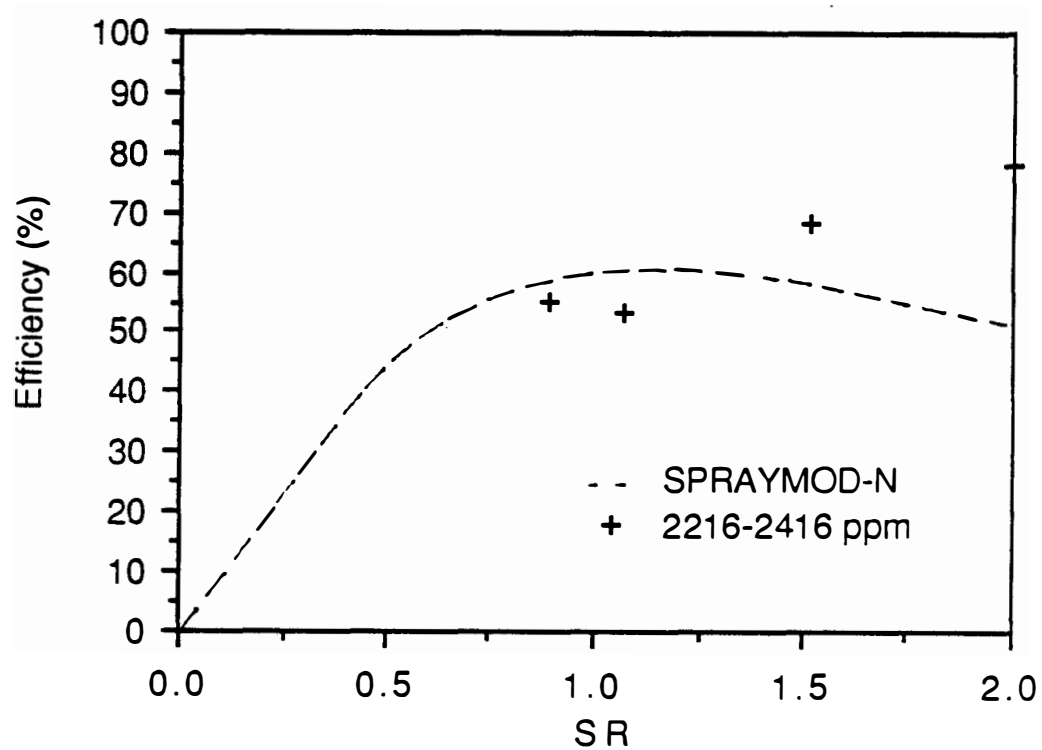


Figure 4-26. Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 6.

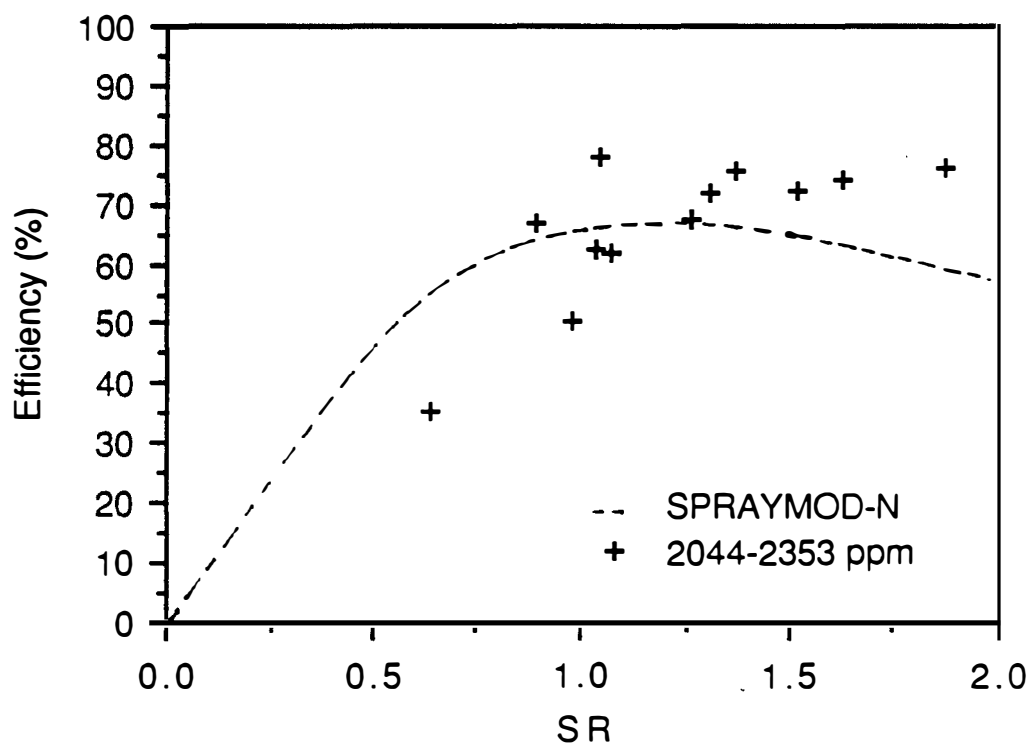


Figure 4-27. Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 7.

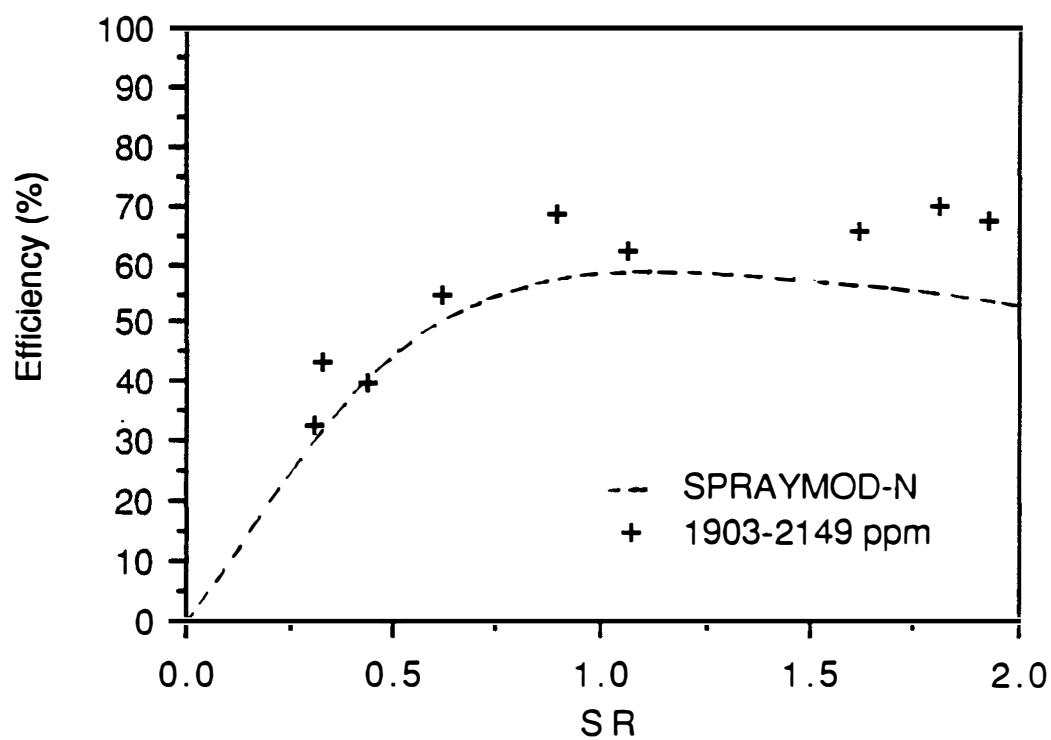


Figure 4-28. Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 8.

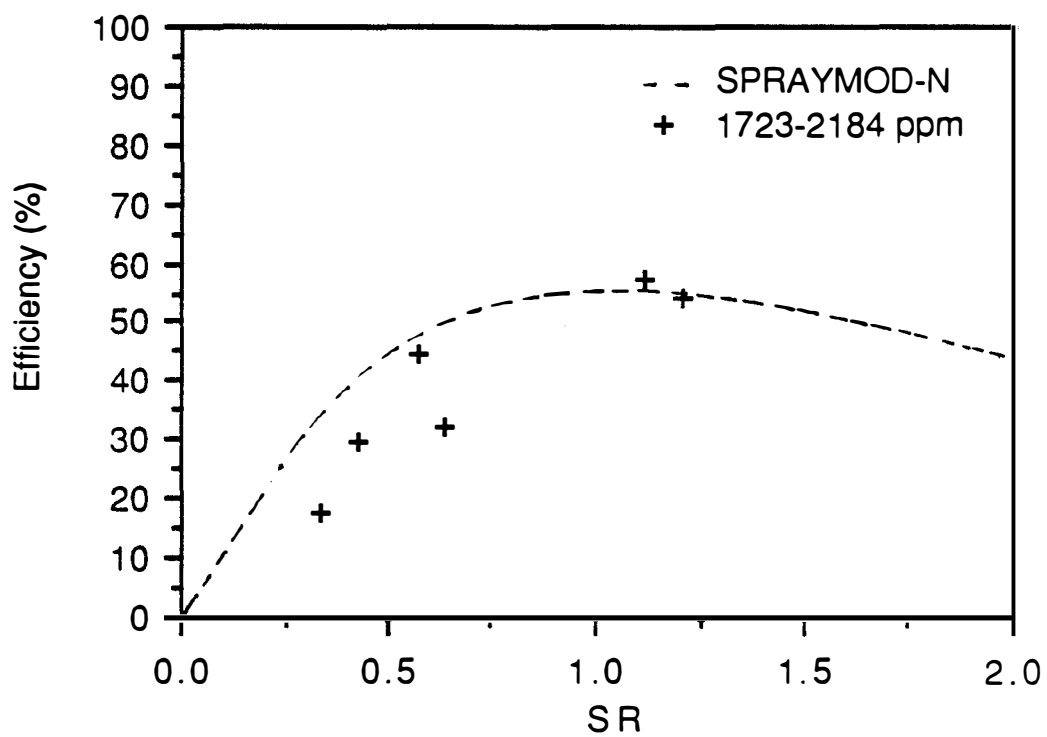


Figure 4-29. Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 9.

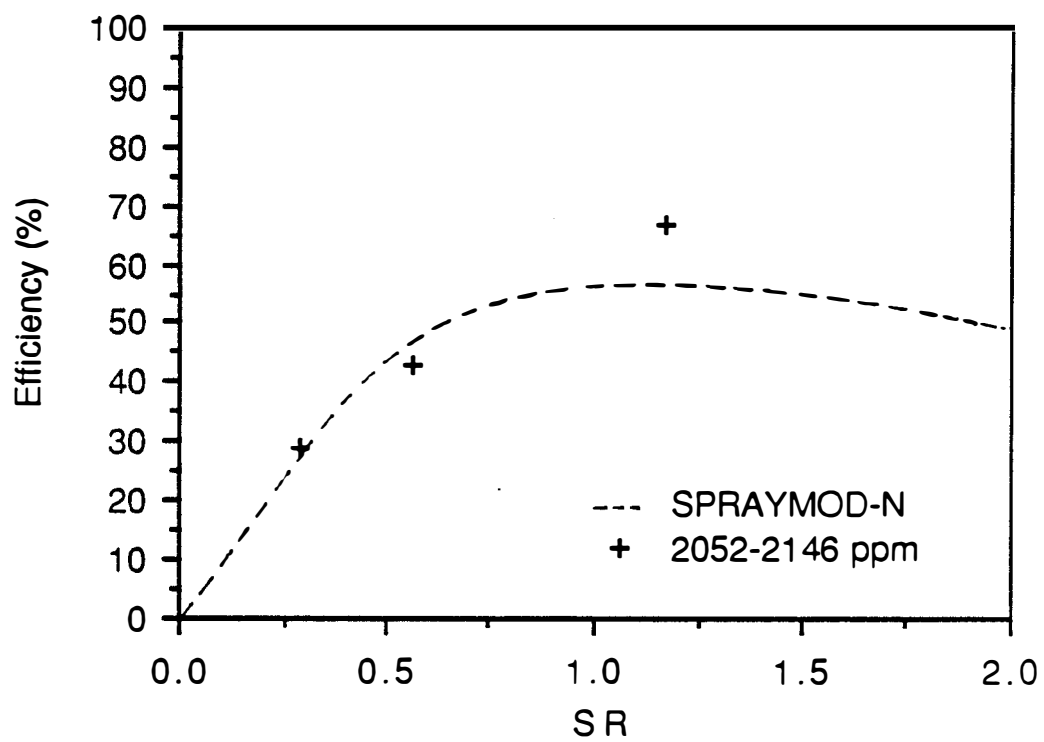


Figure 4-30. Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 10.

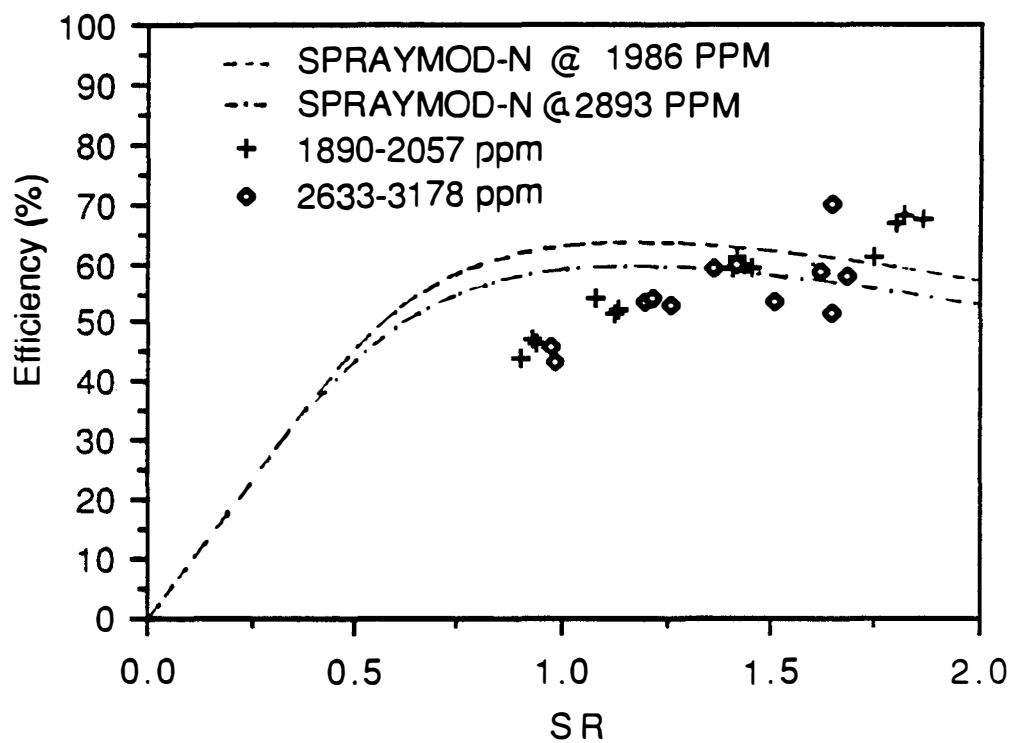


Figure 4-31. Comparison of SPRAYMOD-N predictions with actual pilot plant data for data set 11 and 12.

the gap between actual data and predictions. However, both the versions of the model consider the constant rate period only and so some under prediction is expected. It can be concluded that incorporating measured surface area of the sorbent into the model, rather than estimating from an assumed shape, gives a better prediction. However, this version of the model requires an additional variable (specific surface area) to be measured, which may be a problem for some previous data sets, as most of them may not contain the details about surface area of the sorbent.

CHAPTER V

CONCLUSIONS

In the spray dryer operation using slaked lime slurry for SO₂ removal, slaking aspects are important to obtain good removal efficiencies. The particle size of sorbent Ca(OH)₂ is dependent upon various slaking parameters. This study was made to relate the sorbent characteristics with the removal efficiency. Different sorbent characteristics can be achieved, by adopting various operational methods. The present study produced a reduced particle size of the sorbent by grinding operation. Lime with very little exposure to atmosphere was also studied. Pilot plant tests were run with various slaked lime slurries and compared with each other. A previous mechanistic model was also modified for surface area corrections to input a realistic value rather than a value based on an assumed shape.

Even though laboratory slaking tests showed some differences in the characteristics of slaked slurries of hot lime and regular lime, Ca(OH)₂ from hot lime did not perform as it was reported in an earlier study. It is concluded that the basic raw material may be different for the two sets of samples tested in the two different studies. It is evident that reactivity associated with hot lime tested in previous study can not be achieved on every batch processed in the same manner. The three different batches tested in this work did not perform as reported in the previous study. The calcination conditions might have influenced the reactivity. The conditions were not monitored very closely in either study and so, a definite conclusion could not be drawn. It is found that calcium carbonate formation during air quenching operation is possible only when air with very high moisture content is used. SEM micrographs of Ca(OH)₂ slurries from hot lime and regular lime did not show major variations in the crystal morphology.

Sorbent particle size is found to have a profound effect on the removal efficiency. Slaking conditions dictate the particle size of the resulting slurry. Therefore, controlled slaking

methods are important to achieve desired particle size. Small particle slurries performed well compared to slurries with larger particles. Specific surface areas of the sorbents are measured and related with the removal efficiency. Slaked lime slurry grinding is found to be one of the ways to increase the surface area of the slurry. Spray dryer removal efficiency is observed to increase with the increase in surface area, however there may be a limitation on the maximum achievable efficiency. Although the data showed an increase in efficiency down to 2.4 μm ($\text{SA} = 37.1 \text{ M}^2/\text{G}$) the model suggests that a particle size of below 2.3 microns may not result any further increase in efficiency. It is anticipated that gas-phase resistance controls beyond these conditions. From the model predictions and pilot plant test results, it is anticipated that a maximum lime utilization of around 80 percent in the spray dryer is possible when running with same retention time and at an inlet SO_2 concentration of 1000 ppm, stoichiometric ratio of one and a saturation approach temperature of 20°F . There may be mass transfer limitations due to gas phase resistance beyond the above utilization values. It is also found that grinding of slaked lime slurry requires a large energy input. Benefits attained due to increase in removal efficiency may not be economical on a large scale.

The new version of the model predicted reasonably well for both pilot test data in the present study and previous data collected at the pilot facilities. The measured surface area incorporation into the model resulted in slightly higher predictions compared to the previous versions. In general, the model predicted well for stoichiometric ratios up to 1.25, however there was some under prediction beyond that. This reflects that a model accounting for both falling rate and constant rate periods is essential for the high SR conditions. Model predictions with only constant rate period, fell off for high SR values showing the significance of falling rate period at higher SR values.

The results of this investigation lead one to the conclusion that decrease in sorbent particle size and/or increase in specific surface area (by whatever means) will produce increase

in SO₂ removal across a spray dryer. However, this effect may be truncated when gas phase control is the limiting condition. Therefore, it may not be possible to achieve 100 percent utilization of the sorbent at a SR of 1.0, during the constant rate period of reaction and other enhancements may be needed.

CHAPTER VI

RECOMMENDATIONS FOR FUTURE STUDY

Very high removal efficiencies achieved in the previous study may be due to the presence of sodium or calcium salts. It is recommended to conduct a series of tests involving these salts. Even though their presence may result in higher removal efficiencies, the disposal of waste products may be a potential problem. In the present study efforts were made to obtain a slurry with one micron particles, however it was not successful. Further tests with a one micron slurry are required to conclude any limitations of the mass transfer process. Efforts to link the cost effectiveness of grinding the slurry with additional removal are also recommended. Calcination conditions in the present study may be one of the factors that has caused serious deviation from the previous study. A detailed study involving close monitoring of calcination process is recommended to identify the problem. Regarding the model, further work to model the falling rate period and the dry particle stage will certainly result in a 'complete' model.

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APPENDIX

COMPUTER PROGRAM FOR SPRAYMOD-N

```

10 REM *****
20 REM
30 REM Program - SPRAYMOD-M
40 REM
50 REM      Predicts Efficiency of Sulfur Dioxide
60 REM      Removal in a Spray Dryer using Sorbent Spray
70 REM
80 REM      Program for material and energy balance, sorbent solution,
90 REM      and dry particle reaction stage calculations was developed
90 REM      by: Dr. Ashok S. Damle
100 REM          Research Triangle Institute
110 REM          P. O. Box 12194
120 REM          Research Triangle Park, NC 27709
130 REM
140 REM      Wet particle stage model developed
150 REM      by: George P. Partridge Jr., Wayne T. Davis, and
160 REM          Gregory D. Reed
170 REM          Civil Engineering Department
180 REM          The University of Tennessee
190 REM          Knoxville, Tennessee 37996-2010
200 REM
210 REM      and Robert M. Counce
220 REM      Chemical Engineering Department
230 REM      The University of Tennessee
240 REM      Knoxville, Tennessee 37996
250 REM
260 REM
270 REM      MODEL FOR CONSTANT RATE PERIOD MODIFIED FOR INPUTTING
280 REM      MEASURED VALUE OF SORBENT SURFACE AREA - MAY 88
290 REM
300 REM      SORBENT SPECIFIC SURFACE AREA IN SQ.MET/GM SHOULD BE SUPPLIED
310 REM      THROUGH DATA FILE 'DATA1.BAS'
320 REM
330 REM *****
340 REM
350 REM      START DATA INPUT
360 REM
370 REM *****
380 REM
390 REM      Initialize Default Values
400 PRINT "No. of cases to be calculated? (;N;") - ";:INPUT N
410 CLS:NC=N
420 REM
430 OPEN "DATA" FOR OUTPUT AS #2
440 PRINT #2, NC
450 OPEN "DATA1.BAS" FOR INPUT AS #3
460 II = 0!
470 ZZ = 0!
480 AA=0!
490 BB=0!
500 TI=150:WI=10:AT=10:SI=800:D0=60:DP=4:TW=60:MF=1!
510 MG=28.9:MS=74!:SR=1!:RR=0!:OS=1:MR=.3:SG=2.2
520 XC=50:XE=10:RK=0:RT=10:OP=2:NA$="":MT=.1:PT=.5:SC=.01
530 PRINT "Insert Data Disk in Drive A !"
540 REM SPS1=23
550 PRINT"":PRINT"":PRINT"":PRINT"":PRINT""
560 PRINT"":INPUT"      Enter Datafile Name - (Example:Enter as A:filename) ";E$
570 REM
580 OPEN "I", 1, E$
590 INPUT# 1, NA$,TI,WI,SI,MG,AT,SR,MF,RR,MR,RT,OP,D0,TW,OS,DP,MS,SG,XC,XE,RK,MT
,PT,SC,PI
600 INPUT #3, SPS1
610 PRINT "SURFACE AREA OF LIME =":SPS1
620 II = 0!:AA = 0!:XX=1
630 CC = 0!:BB = 0!
640 REM

```

```

650 P1I = Pi
660 TI=TI+273.15:WI=WI*.01:SI=SI*.000001:LX=(MF+RR*MR)/(1+RR)
670 D0=D0*.0001:TW=TW+273.15:DP=DP*.0001:XC=XC*.01:XE=XE*.01
680 REM
690 REM
700 REM *****
710 REM
720 REM          Calculate Adiabatic Saturation Temperature
730 REM
740 REM *****
750 REM
760 WP=WI*760
770 HI=WP*18!/MG/(760-WP)
780 CS=.24+.45*HI
790 T1=330!
800 L=597.64-.275*(T1+TI-546.3)
810 PS=EXP(20.426-5138.8/T1)
820 YP=PS*18!/MG/(760-PS)
830 E1=TI-T1-(YP-HI)*L/CS
840 IF ABS(E1)<.1 GOTO 1010
850 T2=T1+1
860 L=597.64-.275*(T2+TI-546.3)
870 PS=EXP(20.426-5138.8/T2)
880 YP=PS*18!/MG/(760-PS)
890 E2=TI-T2-(YP-HI)*L/CS
900 IF ABS(E2)<.1 GOTO 1020
910 T3=T1-E1*(T1-T2)/(E1-E2)
920 L=597.64-.275*(T3+TI-546.3)
930 PS=EXP(20.426-5138.8/T3)
940 YP=PS*18!/MG/(760-PS)
950 E=TI-T3-(YP-HI)*L/CS
960 IF ABS(E)<.1 GOTO 1000
970 IF ABS(E1)<ABS(E2) THEN T2=T1
980 IF ABS(E1)<ABS(E2) THEN E2=E1
990 E1=E:T1=T3:GOTO 910
1000 TS=T3:GOTO 1030
1010 TS=T1:GOTO 1030
1020 TS=T2:GOTO 1030
1030 TE=AT+TS
1040 REM
1050 REM *****
1060 REM
1070 REM          Overall Material and Energy Balances
1080 REM
1090 REM *****
1100 REM
1110 PS=EXP(20.426-5138.8/TS)
1120 HS=PS*18!/MG/(760-PS)
1130 TM=(TI+TE)/2
1140 L=597.64-.55*(TM-273.15)
1150 CS=.24+.45*HS
1160 HO=HS-(TE-TS)*CS/L
1170 WO=HO/(HO+18!/MG)
1180 PS=EXP(20.426-5138.8/TE)
1190 RH=WO*760/PS
1200 XU=RH*XE
1210 GW=1.01*(HO-HI)
1220 GS=SI*SR*MS*(1!+RR)/MF/MG/(1!-WI)
1230 ES=SR*(1!+RR*MR/MF)
1240 XF=GW/(GW+GS)
1250 W0=.52356*D0^3*SG/(1!+(SG-1!)*XF)
1260 TN=GW/XF/W0
1270 IF OS=2 GOTO 1360
1280 NP=((D0/DP)^3)*(1!-XF)/(1!+(SG-1!)*XF)
1290 SPS=SPS1*10000
1300 SFA=W0*(1-XF)*SPS

```

```

1310 REM *****
1320 REM
1330 REM      Initialize All Droplet and Gas Phase Variables
1340 REM
1350 REM *****
1360 REM
1370 WW=XF*W0
1380 CM=W0*(1!-XF)*LX/MS
1390 CI=W0*(1!-XF)*(1!-LX)/MS
1400 I = 1!
1410 IF OP=2 GOTO 1490
1420 TG=TI:XW=WI:XS=SI:TD=TW
1430 GOTO 1670
1440 REM
1450 REM      For Backmixed Flow Option Assume SO2 Removal
1460 REM      Efficiency of the Spray Dryer and Calculate
1470 REM      Outlet SO2 Concentration
1480 REM
1490 GOTO 1510
1500 P1=0!:P2=1!
1510 P2=0!
1520 IF ES<1! THEN P2=ES
1530 P1=P1/100!
1540 I=0
1550 REM
1560 REM      Start Trial and Error Sequence to Determine
1570 REM      SO2 Removal Efficiency
1580 REM
1590 I = I + 1!
1600 IF I>1 GOTO 1630
1610 P1=P1*100
1620 P1=P1/100
1630 REM
1640 XS=SI*(1!-P1)*(1!-W0)/(1!-WI):TG=TE:XW=W0:TD=TW
1650 REM
1660 REM
1670 T=0!:TP=0!:ST=0!:D=D0:WD=W0:W=WW:X=XF:UT=0!:
1680 GOTO 3450
1690 REM
1700 REM *****
1710 REM
1720 REM      Solve Material and Energy Balance Equations
1730 REM      for Droplet and Gas Phase
1740 REM
1750 REM *****
1760 REM
1770 TM=(TD+TG)/2!
1780 DS=2.951E-05*TM1.5
1790 DW=5.062E-05*TM1.5
1800 CT=.012194/TM
1810 CO=1.82E-07*TM+.0000079
1820 PW=EXP(20.426-5138.8/TD)
1830 XD=PW/760!
1840 IF XD>1! THEN XD=.9999
1850 IF X<XE THEN XD=X/XE
1860 REM
1870 REM      Rate of Water Evaporation
1880 REM
1890 IF X > XU GOTO 1920
1900 WM=0! : FW=0!
1910 GOTO 1970
1920 WM=6.2832*DW*CT*D*LOG((1!-XW)/(1!-XD))
1930 IF X<XC THEN WM=WM*(X-XU)/(XC-XU)
1940 IF X<XC GOTO 2040
1950 REM DELETE LINE 1820 IF MODELING FALLING RATE DRYING PERIOD
1960 REM LINE 1820 IS (1820 IF X<XC GOTO 1920)

```

```

1970 RL=(CM-ABS(ST))/CM
1980 REM
1990 REM
2000 REM      Check for Dry or Wet State of Droplet
2010 REM
2020 IF X<.01 GOTO 2040
2030 IF X>XU*6.1 THEN GOTO 2230
2040 II = II + 1!
2050 IF II<2 GOTO 2070
2060 GOTO 2120
2070 TNC = I
2080 REM
2090 TDC = T
2100 REM      Rate of SO2 Absorption in
2110 REM      Dry Particle Stage
2120 REM
2130 IF RL>.001 GOTO 2150
2140 SM=0! : GOTO 2160
2150 SM=-RK*XS*CT*RL*CM
2160 FW=WM*18!
2170 FS=SM*64!
2180 GOTO 2730
2190 REM
2200 REM      Rate of SO2 Absorption in
2210 REM      Wet Particle Stage
2220 REM
2230 REM
2240 FW=WM*18
2250 IF RL>.001 GOTO 2290
2260 F=0!:SM=0!:FS=0!
2270 GOTO 2730
2280 REM
2290 IF OS=2 GOTO 2730
2300 VS=(1-X)/(1+(SG-1)*X)
2310 LP=DP:LP=(RL*(LP^3!))^.3333
2320 SFAN=SFA:SFAN=RL*SFAN*(LP^2/DP^2)
2330 CL=.00188-1.174E-05*(TD-273.15)
2340 REM
2350 REM      Calculate Film Thickness
2360 REM
2370 BT=(1!/VS^.333)-1!:FILMT=.5*BT*LP:FILMTL=.5*LP
2380 REM
2390 REM      Calculate Dissolution Rate Reduction due to
2400 REM      Product Precipitation and Inert Solids
2410 REM
2420 RF=1!+(2.108*ABS(ST)+CI)/(CM-ABS(ST))
2430 TCD=TD-273.15
2440 PN=(1.3272*(20!-TCD)-.001053*(TCD-20!)^2!)/(TCD+105!)
2450 DAL=(5.1735E-08*TD)/(1.002*10! PN)
2460 DBL=(5.472E-08*TD)/(1.002*10! PN)
2470 KG=(2!*DS)/D
2480 KAL=DAL/FILMT:KALL=(13.1595*DAL)/D:IF KAL<KALL THEN KAL=KALL
2490 IF TCD>45! GOTO 2520
2500 RHO=1.006615-.0003616*TCD
2510 GOTO 2560
2520 IF TCD>65! GOTO 2550
2530 RHO=1.012141-.000483*TCD
2540 GOTO 2560
2550 RHO=1.020478-.0006102*TCD
2560 IF TCD>45! GOTO 2590
2570 KO=.13846*TCD-.55
2580 GOTO 2630
2590 IF TCD>65! GOTO 2620
2600 KO=.18376*TCD-2.6176
2610 GOTO 2630
2620 KO=.2281143*TCD-5.492191

```

```

2630 KO=KO*(10!4!):IF FILMT>FILMTL THEN FILMT=FILMTL
2640 HA=((2.88745E-04)*(KO-760!))/(RHO*TD)
2650 R=1/(KG*HA)+1/KAL+(3.141593*FILMT*RF*D^2!)/(SFAN*DAL)
2660 C=(CT*XS)/HA+(DBL*CL)/(DAL*MS)
2670 F=-((3.141593*D^2!)*C)/R
2680 SM=F
2690 FS=F*64.06
2700 GOTO 3920
2710 REM          RATE OF HEAT TRANSFER
2720 REM
2730 IF WM=0! AND ABS(TG-TD)<.2 THEN Q=0! :GOTO 2810
2740 EP=1.289*WM/CO/D
2750 IF EP<.00001 THEN EP=.00001
2760 Q=6.2832*CO*D*(TG-TD)*EP/(EXP(EP)-1)
2770 REM
2780 REM          Calculate Derivative Functions and
2790 REM          set Time Step DT
2800 REM
2810 F1=(Q-WM*10080)/WD
2820 F2=-FW-FS
2830 IF F1=0! THEN D1=1000:GOTO 2850
2840 D1=SC*(TD-273!)/ABS(F1)
2850 IF F2=0! THEN D2=1000:GOTO 2870
2860 D2=SC*WD/ABS(F2)
2870 DT=D1
2880 IF D2<D1 THEN DT=D2
2890 IF DT>MT THEN DT=MT
2900 REM
2910 IF OP=2 GOTO 3080
2920 REM
2930 REM          Calculate Change in Gas Phase Variables
2940 REM          ( for OP=1 )
2950 REM
2960 CS=.24+(.446*18!*XW)/(MG*(1!-XW))
2970 DG=Q*DT*TN/CS
2980 TG=TG-DG
2990 SD=SM*DT*TN*(1!-XW)*MG
3000 XS=XS+SD
3010 DX=WM*DT*TN*(1!-XW)*MG
3020 XW=XW+DX
3030 XS=XS/(1!+DX):XW=XW/(1!+DX)
3040 REM
3050 REM          Calculate Change in Droplet Variables during
3060 REM          Time Step DT
3070 REM
3080 T=T+DT
3090 ST=ST+SM*DT
3100 UT=-ST/CM
3110 TD=TD+F1*DT
3120 IF OS = 2 GOTO 3290
3130 REM
3140 REM          For Slurry Option (OS = 1)
3150 REM          Ca(OH)2 + SO2 + H2O = CaSO3.2H2O Reaction is
3160 REM          Assumed and the Change in Weight of Droplet and
3170 REM          Water Content are Calculated Accordingly.
3180 REM
3190 WD=WD+F2*DT
3200 W=W-FW*DT+18!*SM*DT
3210 IF W<0 THEN W=0
3220 GOTO 3330
3230 REM
3240 REM          For Solution Option (OS=2)
3250 REM          Na2CO3 + SO2 = Na2SO3 + CO2 Reaction is Assumed
3260 REM          and the Change in Weight of Droplet and Water
3270 REM          Content are Calculated Accordingly.
3280 REM

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3290 WD=WD+F2*DT+44!*SM*DT
3300 W=W-FW*DT
3310 IF W<0 THEN W=0
3320 REM
3330 X=W/WD
3340 D=((WD+(SG-1)*W)/SG/.52356)^(1!/3!)
3350 REM
3360 REM      Check for Zero SO2 Removal During Last Time Step
3370 REM
3380 IF SM=0! GOTO 3450
3390 REM
3400 REM      Check for End Time and Printout Times
3410 REM
3420 IF T>RT GOTO 3450
3430 IF T<TP GOTO 1770
3440 TP=T+TP
3450 REM
3460 REM
3470 IF T=0 GOTO 1770
3480 IF SM=0! GOTO 3540
3490 IF T>RT GOTO 3540
3500 GOTO 1770
3510 REM
3520 REM      Calculate SO2 Removal Efficiency
3530 REM
3540 EF=ES*UT
3550 IF OP=1 GOTO 3750
3560 P2=EF
3570 IF P2>1! THEN P2=1!
3580 P3=ABS(P1-P2)
3590 IF P3<.02 GOTO 3690
3600 IF I=1 THEN PA=P1:PB=(P1+P2)/2:GOTO 3670
3610 PC=(P1+P2)/2
3620 IF ABS(PC-PB)<ABS(PB-PA) GOTO 3660
3630 IF (PB-PC)/(PB-PA) > 0! THEN PC=(PA+PB)/2
3640 IF (PB-PC)/(PB-PA) < 0! THEN PC=1.5*PB-PA/2
3650 P2=2!*PC-P1
3660 PA=PB:PB=PC
3670 P1=(P1+P2)/2!
3680 GOTO 1580
3690 EF=(P1+P2)/2:XS=SI*(1!-EF)*(1!-WO)/(1!-WI)
3700 REM
3710 REM
3720 CC = CC + 1!
3730 REM
3740 IF CC<2! GOTO 3460
3750 GOTO 3760
3760 REM
3770 REM      Check for Remaining Datasets
3780 REM
3790 N=N-1!
3800 ZZ = ZZ + 1!
3810 IF ZZ>1! GOTO 3840
3820 REM OPEN "DATA" FOR OUTPUT AS #2
3830 GOTO 3850
3840 REM
3850 PRINT# 2, CHR$(34);NA$;CHR$(34);TI,WI,SI,MG,AT,SR,MF,RR,MR,RT,OP,D0,TW,OS,D
P,MS,SG,XC,XE,RK,MT,PT,SC,P1I,TE,TS,WO,RH,TNC,TDC,T,TG,TD,D,X,XW,XS,UT,I,EF
3860 PRINT"No. of cases still to be calculated = ";N
3870 IF N>0 GOTO 590
3880 CLOSE #1
3890 CLOSE #2
3900 CLOSE #3
3910 GOTO 4190
3920 COND=(.1218*SFAN*(DAL^2!))/(FILMT*(D^3!)*(KAL^2!))
3930 IF COND<1! GOTO 4030

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3940 LPRINT" SOLID DISSOLUTION IN LIQUID FILM IS IMPORTANT
3950 LPRINT" MODEL DOES NOT APPLY - N = ";N
3960 LPRINT" COND = ";COND
3970 LPRINT" TIME = ";T
3980 LPRINT" ITERATION = ";XX
3990 IF XX > 1 GOTO 4020
4000 IF XX=1 THEN LPRINT "CONDITION FAILED IN THE FIRST ITERATION"
4010 N=N-1:GOTO 3870
4020 XX=XX+1 :GOTO 3790
4030 REM
4040 GRATE=KG*3.141593*(D`2!)*CT*XS
4050 DRATE=SFAN*(DBL/(FILMT*RF))*(CL/MS)
4060 CONCB=(CL/MS)+((F*FILMT*RF)/(SFAN*DBL))
4070 MODELR=-F
4080 IF GRATE>MODELR GOTO 4130
4090 F=-GRATE
4100 SM=F
4110 FS=F*64.06
4120 GOTO 4170
4130 IF CONCB>0! GOTO 4170
4140 F=-DRATE
4150 SM=F
4160 FS=F*64.06
4170 REM
4180 GOTO 2710
4190 CLS:PRINT "FINISHED ALL DATA SETS AND THE OUTPUT HAS BEEN STORED IN 'data'
FILE AND WILL BE PRINTED SOON"

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VITA

Sambamurty Raju Dantuluri was born on November 15, 1952, in Pippara of West Godavari District in Andhra Pradesh State, India. After his high school studies in Pippara, he went to Andhra Loyola College, Vijayawada, for his Pre-University study. He joined Andhra University, Waltair, from where he received B.Tech and M.Tech degrees in Chemical Engineering. He was employed with A.P.Paper Mills, Rajahmundry, India, for a period of about five years. In the Fall of 1982, he started graduate work in Chemical Engineering program at The University of Tennessee, Knoxville, from where he received his M.S degree in March 1985. He entered the Civil Engineering department at The University of Tennessee, Knoxville, in March 1985 for Ph.D program. He received the Doctor of Philosophy degree in Environmental Engineering program, in December 1988.

The author is a member of Chi Epsilon, APCA and ASCE. He is currently employed with Advanced Waste Management Systems Inc.

The author is married to former Krishna Kumari Kalidindi, and they have two sons, Ravi and Surendra.