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**GLOBAL EVALUATION OF MASS TRANSFER EFFECTS: IN-DUCT
INJECTION FLUE GAS DESULFURIZATION**

Final Report

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FINAL REPORT

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ABSTRACT

Sorbent injection is a low capital cost, low operating cost approach to SO_2 control targeted primarily at older boilers for which conventional fuel gas desulfurization is not economically viable. Duct injection is one variation of this concept in which the sorbent, either a dry powder or a slurry, is injected into the cooler regions of the boiler, generally downstream of the air heaters. The attractiveness of duct injection is tied to the fact that it avoids much of the boiler heat transfer equipment and thus has minimal impact on boiler performance. Since both capital and operating costs are low, the economics of all sorbent injection processes are closely linked to sorbent cost, and, hence to sorbent performance, or reactivity. This program had as its objectives three performance related issues to address:

- 1) Experimentally identify limits on sorbent performance
- 2) Identify and test sorbent performance enhancement strategies
- 3) Develop a computer model of the duct injection process.

Two major tasks are described: a laboratory-scale global experiment and development of process model. Both are aimed at understanding and quantifying the rate-limiting processes which control SO_2 capture by lime slurry during boiler duct injection. The two tasks were conducted interactively in tandem. During the model development, subprocesses were identified which were thought to impact slurry reactivity. These subprocesses were then investigated and, when possible, quantified by the experimental task. Furthermore, the experimental system was well characterized so that the number of uncertainties in the model predictions could be minimized.

The primary conclusions derived from this program are as follows:

- Lime slurry reactivity may be controlled by both internal and external diffusional resistances depending on droplet size and droplet "age."
- The maximum rate of slurry SO_2 capture occurs under external mass transfer control over much of the droplet lifetime.
- Carbonate contamination of the sorbent can increase internal diffusional resistances and reduce slurry reactivity.
- Slurry reactivity can be promoted by the addition of sodium salts, but only if the reaction is under internal mass transfer control. This can mitigate the effects of carbonate contamination.

TABLE OF CONTENTS

<u>SECTION</u>	<u>PAGE</u>
ABSTRACT	ii
ACKNOWLEDGEMENTS	xi
S.0 EXECUTIVE SUMMARY	S-1
S.1 Introduction	S-1
S.1.1 Background and Objectives	S-1
S.2 Experimental	S-7
S.2.1 Results	S-10
S.3 Modeling	S-13
S.3.1 Model Description	S-13
S.3.2 Reaction Control	S-19
S.4 Enhancement Strategies	S-21
S.5 Practical Applications	S-22
S.6 Conclusions	S-26
 PART I EXPERIMENTAL STUDIES	
1.0 INTRODUCTION	1-1
2.0 DESCRIPTION OF THE EXPERIMENT	2-1
3.0 DISCUSSION OF DATA	3-1
3.1 Baseline Test Results	3-1
3.2 Sorbent Variability Studies	3-1
3.3 Alternate Sorbents	3-8
3.4 Slurry Concentration Effects	3-8
3.5 Droplet Diameter	3-12
3.6 SO ₂ Concentration	3-12
3.7 Impact of Sorbent Surface Area	3-12
3.8 Effect of CO ₂ on Slurry Reactivity	3-17
3.9 Droplet Evaporation	3-22
3.10 Enhancement Strategies	3-24
4.0 QUALITY ASSURANCE ISSUES	4-1
5.0 SUMMARY OF FINDINGS	5-1
 PART II IN-DUCT SLURRY DROPLET PROCESS MODEL	
6.0 INTRODUCTION	6-1
7.0 FUNDAMENTALS OF MODEL	7-1
7.1 Slurry Droplet Model	7-1
7.1.1 Single Drop Evaporation	7-6
7.1.2 Gas Phase Temperature	7-8
7.1.3 Particle Scavenging	7-8
7.1.4 Drop Deceleration	7-9
7.1.5 Particle Diffusion	7-10

TABLE OF CONTENTS (CONTINUED)

<u>SECTION</u>	<u>PAGE</u>
7.1.6 Reaction of Sulfur Species with Sorbent Particles in Slurry Drop	7-10
7.1.7 Reaction of Sorbent in Wet Agglomerate	7-12
7.1.8 Reaction of Scavenged Sorbent During Deceleration	7-13
7.1.9 Liquid Phase Diffusion of Sulfur Species	7-13
7.1.10 Liquid Phase Diffusion of Calcium Hydroxide	7-15
7.1.11 Solution of Concentration Profiles	7-16
7.2 Dry Injection/Condensation Model	7-17
8.0 MODEL DESCRIPTION	8-1
9.0 MODEL OPERATION	9-1
9.1 Slurry Injection	9-1
9.1.1 Input	9-1
9.1.2 Operation	9-3
9.1.3 Output	9-3
9.2 Sorbent Injection Followed By Spray	9-4
9.3 Humidification	9-7
9.4 Sorbent Injection After Humidification	9-7
10.0 COMPARISON OF MODEL AND DATA	10-1
11.0 NOMENCLATURE FOR SO ₂ -SLURRY DROPLET MODEL	11-1
12.0 REFERENCES	12-1
APPENDIX 1 LISTING OF COMPUTER CODE	A1-1
APPENDIX 2 MAJOR MODEL VARIABLES	A2-1
APPENDIX 3 EXPERIMENTAL DATA TABLES	A3-1

LIST OF TABLES

TABLE

PAGE

3-1	Physical and chemical analyses of sorbents from the second shipment of Marblehead hydrated lime	3-4
3-2	Chemical analysis of Marblehead AH (commercial) and alcohol hydrate (prepared in-house)	3-19
4-1	Measured in-probe SO ₂ capture (15 minute exposure, 1500 ppm SO ₂) using the oil-heated sampling probe	4-2
10-1	Typical spray size distribution	10-4

LIST OF FIGURES

FIGURE		PAGE
S-1	Effect of approach to saturation on pilot-scale SO ₂ capture from several facilities	S-3
S-2	Description of the Duct Injection Process	S-5
S-3	Diagram of the slurry droplet reactor (SDR) configuration with the settling chamber and heated extractive sampling probe	S-8
S-4	Drop size distribution for water and 20 percent slurry droplets generated by the rotary disk atomizer	S-9
S-5	Effect of slurry concentrations on sorbent utilization at baseline test conditions of 60°C, 1500 ppm SO ₂ , 20 krpm atomizer speed. Data obtained with bag 2	S-11
S-6	Measure calcium utilizations for different bags taken from a single 500 lb shipment of Marblehead hydrated lime	S-12
S-7	Utilization of a lime slurry prepared from a "carefully calcined" lime. The carefully calcined lime was prepared at 950°C under a dry nitrogen atmosphere. Data for the baseline Marblehead hydrate and a freshly slaked Marblehead quicklime are shown also	S-14
S-8	Illustration of the accumulation of sorbent and product at the droplet surface as evaporation shrinks the surface	S-17
S-9	The two types of reaction fronts	S-18
S-10	Relative rate of SO ₂ sorption as a function of droplet initial diameter and relative lifetime	S-20
S-11	Impact of sodium hydroxide and sodium salts on the measured utilization of Marblehead hydrate taken from bag 7. The additives were present at 10 mol percent relative to calcium	S-23
S-12	Impact of 10 mol percent addition o. acids on the measured utilization of Marblehead hydrate taken from bag 7	S-24
S-13	Predicted and measured pilot-scale SO ₂ capture as a function of the normalized stoichiometric ratio of sorbent slurry to SO ₂ . The lower curve shows the predicted impact of 16 percent carbonate contamination of the hydroxide	S-25
2-1	Diagram of the slurry droplet reactor (SDR) configuration with the settling chamber and heated extractive sampling probe	2-2

LIST OF FIGURES (CONTINUED)

<u>FIGURE</u>		<u>PAGE</u>
2-2	Drop size distribution for water and 20 percent slurry droplets generated by the rotary disk atomizer	2-4
3-1	Baseline sorbent utilization measured using bag 2 of the second shipment of Marblehead calcium hydroxide	3-2
3-2	Measure calcium utilization for different bags taken from a single 500 lb shipment of Marblehead hydrated lime	3-3
3-3	Correlation between measured utilization and carbonate content of calcium hydroxides. The curve through the data is a model made assuming that the carbonate content correlates with availability of carbonate surface area . .	3-6
3-4	Utilization of a lime slurry from a "carefully calcined" lime. The carefully calcined lime was prepared at 950°C under a dry nitrogen atmosphere. Data for the baseline Marblehead hydrate and a freshly slaked Marblehead quicklime are shown also	3-8
3-5	Comparison of alternative sorbents reactivity under baseline test conditions	3-10
3-6	Effect of slurry concentrations on sorbent utilization at baseline test conditions of 60°C, 1500 ppm SO ₂ , 20 krpm atomizer speed. Data obtained with bag 2	3-11
3-7	Slurry concentration dependence of sorbent utilization at baseline test condition of 60°C, 1500 ppm SO ₂ , 20 krpm atomizer speed. Data obtained with bag 2	3-12
3-8	Impact of drop size on slurry reactivity. Triangles are data for 70 μm mmd droplets. Data obtained using bag 4	3-13
3-9	Sorbent utilization measured at 100, 500, and 1500 ppm SO ₂ . Data obtained using bags 2 and 3	3-14
3-10	Impact of SO ₂ concentration on measured sorbent utilization at different sampling distances. Data obtained using bags 2 and 3	3-16
3-11	Impact of high SO ₂ concentration on slurry utilization with Bag 4 of the Marblehead AH	3-17
3-12	Difference in reactivity between a commercial hydrated lime (Marblehead, 15 m ² /g) and an in-house prepared high surface area hydrated lime (50 m ² /g). Experiments were carried out at baseline test conditions	3-18

LIST OF FIGURES (CONTINUED)

<u>FIGURE</u>		<u>PAGE</u>
3-13	Utilization of Marblehead AH slurries containing 1.25% and 4.75% v/v methanol. Tests with methanol and baseline curve shown were obtained using bag 5	3-21
3-14	Impact of CO ₂ on baseline sorbent utilization using bag 4	3-22
3-15	Data and model predictions for evaporating and non-evaporating cases. All data obtained using bag 2. Non-evaporating data were obtained at the baseline condition. Evaporating data were obtained with only ambient moisture levels (approx. 90°C approach to saturation)	3-23
3-16	Impact of 10 mol percent addition of acids on the measured utilization of Marblehead hydrate taken from bag 7 . . .	3-26
3-17	Impact of sodium hydroxide and sodium salts on the measured utilization of Marblehead hydrate taken from bag 7. The additives were present at 10 mol percent relative to calcium	3-27
4-1	In-probe SO ₂ capture test results compared with baseline . .	4-3
7-1	Illustration of the accumulation of sorbent and product at the droplet surface as evaporation shrinks the surface .	7-3
7-2	The two types of reaction fronts	7-4
8-1	Flow chart of model	8-2
9-1	Sample listing of input data file	9-2
9-2	Model output for the input data file given in Figure 9-1 . .	9-5
9-3	Model output for the input data file given in Figure 9-1 with input parameter λ changed to the letter "a"	9-6
9-4	Sample listing of input data file	9-8
9-5	Model output for the input data file given in Figure 9-4 . .	9-9
10-1	Relative rate of SO ₂ sorption as a function of droplet initial diameter and relative lifetime	10-2
10-2	Prediction and measured pilot-scale SO ₂ capture as a function of the normalized stoichiometric ratio of sorbent slurry to SO ₂	10-3

LIST OF FIGURES (CONTINUED)

FIGURE

PAGE

10-3	Model predictions compared with pilot-scale data showing the impact or approach to saturation of in-duct injection slurry utilization	10-5
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S.0 EXECUTIVE SUMMARY

S.1 Introduction

In-duct flue gas desulfurization is a process in which sorbent materials are injected into the exhaust duct of a power plant at a location downstream of the air heater. Under high humidity, calcium-based sorbents are capable of capturing significant amounts of SO_2 . Since the sorbents are never injected into the boiler, problems associated with fouling are avoided, as are other interferences with boiler operation.

The low capital cost causes the process economics to depend largely on the sorbent costs. Thus, there is considerable motivation to improve sorbent reactivity. Sorbent utilization therefore becomes a key parameter in establishing the competitiveness of duct injection.

In this project, fundamental droplet experiments are combined with a model to identify the rate controlling steps, and to develop reactivity enhancement strategies. The results indicate that both internal and external transport control are dominant during various portions of the droplet lifetime. Certain reactivity limitations imposed by internal control can be overcome by enhancement approaches.

S.1.1 Background and Objectives

At present, a number of SO_2 control technologies are under development or demonstration for application to utility boilers. Although wet scrubbing removes sulfur with high efficiency, its high cost and its generation of a slurry waste have motivated many to look for lower cost alternatives. Among the areas receiving considerable attention are the use of inexpensive calcium-based sorbents. These are designed to be passed through the system once and thrown away. Their goal is to achieve moderate SO_2 control at a low cost. The target is usually older plants where the high capital cost of scrubbers could not be economically justified. Thus, the economics of these calcium-based processes are

dominated by sorbent cost, and one key to reducing cost is to increase the utilization of the sorbent (i.e., its conversion to sulfate product).

The injection of limestone or calcium hydroxide into the upper furnace to capture SO_2 via a sulfate formation mechanism has been studied extensively, and has progressed to the demonstration phase (1). In another process, calcium hydroxide is injected into the economizer region to capture sulfur as CaSO_3 (2). The third major process is the injection of calcium hydroxide, in either dry or slurry form, after the air heater. This process has been termed "Duct Injection."

Duct injection has adopted several forms. In one form, it consists of the injection of hydroxide slurry directly into the duct. An alternate form is to inject dry hydroxide into the duct and humidify the duct with a separate water spray nozzle. The humidification can occur either before or after the dry hydroxide injection.

Assuming appropriate sorbent utilizations, the advantages of duct injection are obvious. No furnace penetrations are required. No sorbent is injected into the furnace, where it can interfere with the heat transfer. Lastly, the performance of furnace injection depends strongly on placing the sorbent into the furnace at the correct temperature. Furnace turndown can move this thermal window within the boiler, and result in reduced performance. By its nature, duct injection is less severely affected by changes in the boiler load.

Duct injection has been examined at bench-and pilot-scale in a number of studies. These include studies by CONOCO (3). EPRI (4), Babcock and Wilcox (5), Dravo (6), and General Electric (7). Figure S-1 presents a compilation of these data. This shows the two most important observations arising from duct injection experiments. First, the sorbent utilization responds most strongly to the relative humidity of the duct. High utilization is possible, but generally only if the duct is humidified below a 30°F approach to adiabatic saturation. These high levels of humidification can lead to operational problems due to long

Figure S-1. Effect of approach to saturation on pilot-scale SO₂ capture from several facilities.

evaporation times required for droplets, and formation of deposits from the sticky, humid solids.

The other observation from Figure S-1 is that slurry injection (including the spray dryer data) show much higher performance than the dry injection/separate humidification data. This illustrates the importance of good contacting between the humidification water and the sorbent in promoting reactivity.

The reactivity of hydroxide sorbents has been extensively characterized in fixed-bed experiments. These studies have shown that even under conditions of high equilibrium moisture content, the sorbents will collect sulfur only if given many minutes for reaction. This is much too slow to account for the captures that are observed within the 1-2 seconds available for reaction in the dispersed-phase pilot-scale experiments. This leads to the hypothesis that significant dispersed-phase capture can only occur if the sorbent is physically wetted - equilibrium moisture adsorption is simply not sufficient. In Figure S-1, higher captures are observed for the preslurried sorbents because each sorbent particle is physically wetted. For the dry injection cases, only particles that are wetted by initial impaction with droplets (8,9) or are wetted by bulk condensation (10) will become reactive. Based on this explanation, it is clear that the slurries outperform dry injection because all of the sorbent particles are wetted.

The other hypothesis to be drawn from these data is that a close approach to saturation prolongs the evaporation time of the physically wetted droplets, extending their reactive lifetime.

Figure S-2 outlines a general understanding of the mechanisms involved in the duct injection process. If the sorbent is injected dry, it can become wetted through inertial impaction with the water spray. If the duct is pre-humidified and the sorbent is injected dry at room temperature (cold), then the sorbent can collect a significant layer of condensate. If the sorbent is injected as a slurry, then these wetting steps are unnecessary.

Figure S-2. Description of the Duct Injection Process.

The capture of sulfur by the slurry droplet is controlled by a number of rate processes. Initially, the lifetime available for reaction will be governed by the droplet size and the local relative humidity. The reaction rate itself will be governed by:

- The rate transport of sulfur to the external surface of the droplet.
- The rate at which dissolved calcium becomes available within the droplet due to the dissolution of the hydroxide.
- The rate of dissolution and transport of sulfur within the liquid phase.
- The rate of reaction, and the potential binding of hydroxide surfaces by the insoluble product.

At present, evaporation times, and external transport rates can be calculated with confidence. The greatest unknowns are the mechanisms governing the internal reaction.

Two major challenges face the implementation of the duct injection process. First, bench- and pilot-scale tests have shown that the close approaches to saturation that are needed to promote good reactivity can lead to operational problems. Specifically, the ducts are prone to deposit buildup, and unevaporated droplets can carry over into the ESP. Thus, it would be desirable to avoid very close approaches to saturation. The second challenge is to improve the reactivity of the sorbent. In such a low capital cost process, the economics are heavily weighed towards the unit cost of the sorbent, and the amount of sorbent needed to get a desired amount of capture. Improvements in sorbent reactivity translate directly into reduction in total operating cost.

The objectives of this project are to identify the factors that govern the rate of sulfur capture by slurry droplets. When identified, these rates are to be used to select and test enhancement strategies. A fundamental experiment that

investigated the reaction of individual slurry droplets is the heart of the study. A model was concurrently developed to (1) interpret the data from the fundamental experiments, and (2) provide a tool for extrapolating the findings to practical scale.

S.2 Experimental

The experiment was designed to generate droplets of calcium hydroxide slurry of known size and solids content, to expose them to SO_2 -containing gases for a known amount of time, and to collect the products to determine the conversion of the calcium to product. The slurry reactor consists of a rotary disk atomizer placed on top of a laminar flow reactor. Gas flow to the reactor is provided by a flat flame burner fired on methane fuel.

A diagram of the reactor is shown in Figure S-3. The rotary disk atomizer is 12.5 cm in diameter and operates at 10,000 to 20,000 RPM. The slurry is fed to the center of the disk and flows to the rim where the droplets are generated. A series of skimmers select a small fraction of the droplets, which pass into the settling chamber. The settling chamber permits the slurry droplets, which have an initial velocity on the order of 130 m/s, to relax their terminal velocities before entering the reaction zone. As the droplets settle into the reactor they are entrained into the flue gas by mixing vanes which provide a temporary turbulent zone near the reactor entrance.

An important experimental parameter is the size distribution of the slurry droplets. This is affected mainly by the rotation speed of the atomizer. Drop size characterization results are shown in Figure S-4 from laser diffraction measurements. The data indicate that the differences between slurry and pure water are slight. The rotor speed of 20,000 RPM was selected as the baseline operating condition. This provided a 32 μm mass-median droplet diameter with 80 percent of the droplet mass between 6 and 52 μm .

The lime slurry was prepared from a commercial hydrated lime obtained from Marblehead Lime company. The slurry was prepared in 5 gallon lots and was

Figure S-3. Diagram of the slurry droplet reactor (SDR) configuration with the settling chamber and heated extractive sampling probe.

Figure S-4. Drop size distribution for water and 20 percent slurry droplets generated by the rotary disk atomizer.

filtered to remove sand and coarse particles. The slurry concentration was verified by specific gravity measurements.

Solid samples were collected with a hot-oil probe. A pump circulated oil at 230°C through the probe and filter housing. This flash vaporized all droplets entering the probe so that further in-probe capture was minimized. The level of in-probe capture was checked by collecting samples in a sulfur-free environment and subsequently exposing them to SO₂-containing flue gases. The collected solids were analyzed for their calcium and sulfur content by dissolving the sample in HCl and oxidizing it with hydrogen peroxide. After this they were neutralized with NaOH, and aliquots were analyzed by inductively-coupled argon plasma atomic emission spectroscopy for Ca⁺⁺ and ion chromatography for SO₄⁻⁻.

S.2.1 Results

Results were obtained for a wide range of operating parameters. These include: reactor temperature, evaporating vs. non-evaporating conditions, droptime, slurry concentration, solids particle size, solids specific surface area, presence or absence of CO₂ in the reactor atmosphere, and sorbent type.

The data in Figure S-5 show the slurry utilization vs. time for the baseline reactor operating condition and variable slurry concentrations. Figure S-5 shows that the differences in slurry concentration were greatest for the shortest residence times. All of the data, except that for the 1 percent slurry tended to converge at long times. In fact, slurry concentration has only a small effect until the concentration is reduced to below 5 percent.

Sorbent type had one of the more marked influences. Figure S-6 compares calcium utilizations measured from several batches of commercial hydroxide from the same supplier. Batches 2 and 3 both show utilizations over 60 percent at long times. The later batches showed maximum utilizations not exceeding 42 percent. This represented a large change in the reactivity of the base material for no apparent reason.

Figure S-5. Effect of slurry concentrations on sorbent utilization at baseline test conditions of 60°C, 1500 ppm SO₂, 20 krpm atomizer speed. Data obtained with bag 2.

Figure S-6. Measure calcium utilizations for different bags taken from a single 500 lb shipment of Marblehead hydrated lime.

Analysis of the samples suggested that the poor behavior of some of the sorbents was due to partial carbonation of the materials. This was tested in two ways: first, by carefully calcining a batch of the hydroxide from bag 7 until all the carbonate and hydroxide had been converted to oxide. The oxide was held under nitrogen from the start of calcination, through the slaking process, to the point of injection into the rotary atomizer. Second, a batch of slurry was prepared by slaking a sample of quicklime obtained from Marblehead. Figure S-7 shows that the freshly slaked material yielded a reactivity comparable to the bag 7 baseline results. Meanwhile, the "carefully calcined" material displayed a much higher reactivity, though still lower than that of the first batches of sorbent.

This indicates that carbonate contamination, and possible other sorbent properties, can exert a significant influence on reactivity. For carbonate contamination this could result from blinding of the surface with unreactive insoluble material. The overall reactivity, however, will be governed by the intercoupling of all the rate processes, both external and internal. This intercoupling is so complex that only a mathematical model is capable of finding (1) whether enhancement strategies for an individual rate step will result in improved practical performance, and (2) whether sorbent deactivation, such as carbonate blinding, will harm overall performance. Thus, the development of a model that permits extrapolation of the results to full scale is a critical part of the program.

S.3 Modeling

S.3.1 Model Description

A number of models of SO_2 capture by dry sorbent and slurry droplets have been developed. The model of Jozewicz and Rochelle (11) assumes external transport is controlling. Karlsson and Klingspor (12) developed two models of SO_2 capture: one assumes that external transport controls while the other is based on the calcium dissolution rate. Damle and Sparks (13) included a lime dissolution rate based on film theory applied about each sorbent particle. They

Figure S-7. Utilization of a lime slurry prepared from a "carefully calcined" lime. The carefully calcined lime was prepared at 950°C under a dry nitrogen atmosphere. Data for the baseline Marblehead hydrate and a freshly slaked Marblehead quicklime are shown also.

assumed that bulk transport within the liquid phase was fast. Harriott and Kinzey (14) assumed that sorbent particles do not circulate within the droplet and that the reaction between dissolved calcium and sulfur occurs at a spherical front which progresses inward from the droplet surface only after sorbent particles at the front have been consumed. Their model assumes that sorbent dissolution is fast.

The present model considers the possibility that calcium may dissolve and diffuse out from the center of the droplet. Comparison of the concentrations and diffusivities of liquid phase sulfur and calcium species reveals that their diffusional rates will be on the same order and that the outward diffusion of calcium may be important. The present model addresses these processes.

The model makes the following assumption:

- The liquid phase ionic reaction between dissolved calcium and sulfur species is instantaneous.
- Water and sorbent particles do not circulate within the droplet.
- Changes in the liquid phase concentration profiles occur slowly enough so that the pseudo-steady-state assumption is valid.
- The heats of reaction and sorbent dissolution are small and can be ignored.
- Thermal gradients within the droplet can be ignored.
- The droplets are spherical.

The sulfur capture model described here is coupled with a detailed one-dimensional model of the duct injection process. The duct injection model considers changes in the velocity of droplets when injected into the duct, droplet temperature, evaporation, gas temperature, gas humidity, and scavenging

of particulate matter (ash or sorbent) from the gas phase. The model considers a spray with a distribution of drop sizes. The disposition of sorbent particles during evaporation will influence the rate of internal processes.

If sorbent circulates freely, then the droplet can be viewed as a mixed reactor, while if circulation is minimal, then significant diffusional resistances may have to be overcome. Work by Constan and Calvert (15) and Kinzey (16) indicate that internal circulation within slurry droplets is not significant. Initially the sorbent particles are viewed as being uniformly distributed throughout the droplet. As water evaporates from the droplet, its surface will recede and collect particles which were initially near the droplet surface. Figure S-8 shows the accumulation of particles as the droplet evaporates. The particle concentration gradient created by this evaporation drives an inward transport of particles. While included in the model, this effect is not significant.

Several researchers (17-19) have found that the liquid phase reaction is fast compared to the diffusional processes involved. Two types of reaction fronts can therefore occur within the liquid. The first is a local reaction front that surrounds individual sorbent particles, and the second is a bulk reaction front. These are illustrated in Figure S-9. The model internally balances all the fluxes such that it automatically determines the location of the reaction fronts. For example, the bulk reaction front shown in Figure S-9 can be located 1) at the droplet surface, 2) at some intermediate point within the droplet, or 3) it may not exist at all (i.e., sulfur will penetrate to the center of the droplet). Reaction fronts around the individual sorbent particles will only form if liquid phase sulfur species are present in the local liquid phase.

Evidence is offered by Moyeda et al. (8) that the specific surface area of a sorbent may influence the extent of its utilization. The rate at which an individual sorbent particle dissolves will therefore depend on the rate at which calcium hydroxide leaves the sorbent particle surface and diffuses to the bulk liquid phase where the reaction occurs. This is determined by how close the sorbent particles are together, and the proximity of the reaction front. A

Figure S-8. Illustration of the accumulation of sorbent and product at the droplet surface as evaporation shrinks the surface.

Figure S-9. The two types of reaction fronts.

roughness factor accounts for the non-spherical shape of the sorbent particles, and is allowed to change as the particles dissolve.

The liquid phase diffusion of sulfur is governed by serial processes. The transport of SO_2 to the droplet surface is governed by common film theory. Local equilibrium is assumed to prevail at the droplet surface, and the liquid phase concentration at that location is calculated using a Henry's law constant. The dissolved SO_2 is assumed to rapidly equilibrate to form H_2SO_3 , HSO_3^- and SO_3^{--} . The concentration of SO_3^{--} is negligible and is ignored. Transport equations are written for both H_2SO_3 and HSO_3^- . A transport equation is also written for the diffusion of calcium hydroxide away from the droplet interior.

During solution the program monitors the relative fluxes of the sulfur and calcium species and determines the location of the bulk reaction front. Product is assumed to accumulate as $\text{CaSO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ at the location where reaction occurs. This solid can then interfere with diffusion.

S.3.2 Reaction Control

Exercise of the model shows that both internal processes and external transport can control droplet reactivity, depending on drop size, reaction conditions, and droplet fractional lifetime. Consider Figure S-10, which shows the calculated rate of sulfur absorption divided by the maximum possible rate of external mass transfer. This is shown as a function of relative droplet lifetime (time to complete evaporation). Thus, a value of unity on the ordinate suggests that there is no internal resistance to reaction, and all the resistance is in the gas film surrounding the droplet.

Initially the droplet contains a uniform dispersion of hydroxide particles. The sulfur must diffuse through the liquid near the surface of the droplet to reach a sufficient amount of sorbent to be absorbed. This leads to the initial condition in which the liquid-phase resistance contributes. As the droplet evaporates, the sorbent near the surface becomes swept up by the receding surface. This results in a significant concentration of sorbent particles near

Figure S-10. Relative rate of SO_2 sorption as a function of droplet initial diameter and relative lifetime.

the droplet surface. Now, the sulfur has very little distance to diffuse through the liquid to reach free calcium. At this point in the droplet lifetime the liquid phase processes become fast and the external film resistance becomes rate controlling. This situation prevails until the sorbent near the surface becomes highly utilized. Then the sulfur must diffuse into the droplet interior to reach fresh sorbent. At this point internal transport becomes controlling again, and the overall rate falls below the maximum available from external film control.

S.4 Enhancement Strategies

One implication contained in Figure S-10 is that internal enhancement can contribute to improved utilization, but only up to the point where external transport control becomes important. Thus, as in the earlier example of carbonate blinding, there may be situations in which reactivity can be harmed, but not enhanced. If reactivity is promoted to the point at which external transport becomes the dominant controlling factor, then the only means of further promotion is to increase external transport. The only practical means of accomplishing this is to decrease the droplet size. This, however has the negative effect of decreasing droplet lifetime, which essentially cancels the improvement due to enhanced external transport. Thus, the most direct approach to enhancement is to ensure that as little internal resistance as possible interferes with the reaction. Given this scenario, a number of enhancement strategies were experimentally tested.

Figure S-10 shows that the key to enhancement is to eliminate the regions where the reaction rate is lower than the external transport limit. The situation is complicated by the fact that for some situations the reactivity is already near the maximum allowed by external transport, and no internal enhancement will help.

The model shows that the reactivity can be expected to improve if the liquid phase concentration of the diffusing species can be increased. Sodium hydroxide was selected as a promoter of sulfur solubility, and therefore the sulfur diffusion rate. Several acids were selected to promote calcium

solubility, and sodium salts were used to promote the solubility of both sulfur and calcium species.

Figure S-11 contains several important features. These data were collected by adding the respective sodium compounds to the baseline slurry to the extent of 10 mole-percent relative to the calcium. Note that a complete utilization of the added sodium would increase the apparent calcium utilization only 5 percent. All of the sodium compounds promote the reactivity of the baseline hydrate by considerably more than this amount. Also, there seems to be little difference in performance between the salts and the sodium hydroxide.

Note that Figure S-11 shows that the baseline hydrate is promoted to a level consistent with the freshly slaked nitrogen-calcined hydrate shown in Figure S-7. This suggests that the sodium acts to either (1) avoid the deactivation due to carbonate binding, or (2) to bring the utilization up to the maximum level allowed by external mass transfer, i.e., about 60 percent.

Figure S-12 shows that both formic acid and acetic acid had little influence on the reactivity of the baseline hydrate slurry. This suggests that promotion of calcium solubility has little influence on enhancing the overall reaction under these conditions.

S.5 Practical Applications

The two principal goals of the program were to first, develop a process model of the duct injection process, and second, to suggest means by which the process could be enhanced. The laboratory scale data generated herein provide a means of calibrating the model, but the actual value of the findings can only be realized when the model is exercised against field data.

Figure S-13 shows data and predictions for pilot-scale duct injection. The comparison is good at all conditions. If the internal availability of calcium is assumed to be impaired by the presence of carbonate, then fundamental reactor data can be used to calibrate a blinding factor into the model. This blinding

Figure S-11. Impact of sodium hydroxide and sodium salts on the measured utilization of Marblehead hydrate taken from bag 7. The additives were present at 10 mol percent relative to calcium.

Figure S-12. Impact of 10 mol percent addition of acids on the measured utilization of Marblehead hydrate taken from bag 7.

Figure S-13. Predicted and measured pilot-scale SO₂ capture as a function of the normalized stoichiometric ratio of sorbent slurry to SO₂. The lower curve shows the predicted impact of 16 percent carbonate contamination of the hydroxide.

factor can then be applied to the full scale data shown in Figure S-13. The results show that the moderate amount of carbonate contamination found in the commercial hydrate should substantially reduce reaction in a practical situation. This suggests that some of the variations observed between various materials in practical systems could be due to interferences in sorbent availability. However, these interferences would only be observed in situations where internal reaction control was dominant, e.g., for small droplets. Also, use of promoters can be expected to improve this situation, but only to the point where external mass transport control becomes dominant. Beyond this, internal promoters will yield no improvement in performance.

The latter point may be one explanation why sodium promoters are sometimes observed to produce an increase in sulfur capture that corresponds to the sulfation of the added sodium, and in other cases the incremental capture is beyond stoichiometric. In some experiments external transport will be dominant and the sodium will not promote capture, only react with SO_2 itself. In other situations, the sodium will improve the performance of the calcium when the reaction is under internal transport control.

S.6

Conclusions

The principal conclusions of this study are as follows:

- Accurate modeling of the duct injection process requires consideration of both external transport and internal diffusional resistance.
- The internal diffusional resistance is made up of both calcium- and sulfur-dominated resistances.
- Different resistances become important in different portions of a droplet lifetime. Within a polysized spray., different sized droplets will emphasize different resistances. Thus, a distribution of drop sizes must be considered to model a practical system.

- Carbonate contamination can increase the internal resistance to reaction, and thus reduce performance.
- Promotion by sodium salts provides a means of overcoming internal resistances. This will, however, only work if the droplet being promoted is already under internal transport control. If the control is external, then sodium will yield little apparent improvement.

S.7 References

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PART I EXPERIMENTAL STUDIES

1.0 INTRODUCTION

Part I describes the experimental results from a global investigation of in-duct SO_2 capture by lime-slurry sprays. The purpose of this investigation was twofold. To a large extent the experiments were guided by the parallel model-development effort described in Part II of this report. The data were used to test and refine various assumptions made by the model about internal vs. external mass transfer, temperature, humidity, SO_2 concentration and slurry concentration. Also, the experiments performed a scoping function for the overall DOE duct injection program. By testing lime slurry sprays for SO_2 capture over a range of conditions, this program has identified limits and variabilities of sorbent performance which may be encountered in future pilot- and demonstration-scale tests.

A significant fraction of the experimental effort was applied to a continual evolution of the system design. This evolution of design was a response to the changing needs of the program. These were defined both by the modeling effort and the understanding of the important process parameters which developed as the experimental database increased. Aspects which were especially critical were the slurry atomizer design, the sampling system, and control of the complete reactor environment, including temperature, humidity, and gas composition.

Key findings of the experimental study are as follows:

- 1.) The experiments support the model's contention that the maximum rate of SO_2 capture by lime slurry is controlled by gas-phase diffusion of SO_2 .
- 2.) Handling of the lime after calcination can be a key factor in determining slurry reactivity. Sorption of atmospheric CO_2 either before or after slaking can severely reduce the slurry utilization. This effect is strong enough to mask most other experimental

variables. This may also account for much of the range of reactivities observed between sorbents from different sources.

- 3.) Lime utilization is increased at lower slurry solids concentrations.
- 4.) Increasing hydrate surface area above $15 \text{ m}^2/\text{g}$ does not itself increase lime slurry utilization.
- 5.) Reactivity promoters -- sodium salts in particular -- can mitigate the effects of CO_2 sorption. But it was not possible to increase the slurry reactivity beyond the level predicted by the model at the limit of external mass transfer control.

Slurry reactivity experiments were conducted in EER's Slurry Droplet Reactor Facility (SDR). The SDR (Figure 2-1) consists of a rotary disk atomizer placed on top of a laminar flow reactor. Gas flow to the reactor is provided by a flat-flame burner with methane fuel. The baseline SO_2 concentration is 1500 ppm and the dew point is 60°C . The atomizer delivers a slurry spray to the reactor where it mixes with the burner gas and reacts with SO_2 . Dried slurry samples are collected on a Gelman A/E filter at the base of an oil-heated sampling probe. The oil-heated probe heats the entrained gas stream to 180°C in 30 ms. This effectively flash evaporates the slurry droplets, rendering them unreactive toward SO_2 .

During the course of the program, the experimental system design was continually evolving. This was in response to the experimental demands, and in order to accommodate the level of control required to test model assumptions. The oil-heated sampling probe is an example of such a change. The previous sampling system consisted of passive collection of slurry spray in a heated cup. The need for greater analytical accuracy, hence, longer samples, demanded a larger volume sampling system with the capability to flash evaporate the slurry droplets. At the start of this phase of experimental activity the SDR was modified by the addition of a settling chamber placed between the disk atomizer and the reactor. The settling chamber permits the slurry droplets, which have an initial velocity of 130 m/s, to relax to their terminal velocities before entering the reaction zone. As the droplets settle into the reactor they are entrained into the flue gas by mixing vanes which provide a temporary turbulent zone near the reactor entrance. Toward the end of the experimental program modifications were made to provide better positive control over reactor temperature and the temperature and humidity of the flue gas. This was accomplished by water jacketing the reactor and passing the flue gas through tube-and-shell heat exchangers. These two systems were linked through a controlled-temperature water reservoir providing $\pm 1^\circ\text{F}$ process control.

An important experimental parameter is the size distribution of the slurry droplets. This is affected mainly by the rotation speed of the atomizer. Drop size distribution was measured using a Malvern 26000 HSD laser-diffraction drop

Figure 2-1. Diagram of the slurry droplet reactor (SDR) configuration with the settling chamber and heated extractive sampling probe.

size analyser. This instrument determines the size of droplets by measuring the diffraction-angle/intensity spectrum which results when a collimated laser beam passes through a spray. Drop size characterization results are shown in Figure 2-2. The data shown were obtained for a 20 percent slurry and for pure water. The differences between slurry and water are slight, and indicate that slurry concentration will have little impact on the drop size distribution. The important feature of these data is that they show a significant effect of atomizer rotor speed on slurry drop size. A rotor speed of 20,000 rpm was selected as the baseline operating condition. This provided a 32 μm mass median droplet diameter with 80 percent of the droplet mass between 6 and 52 μm .

The lime slurry was prepared from a commercial hydrated lime obtained from Marblehead Lime Company. The hydrate is shipped in 50 lb. bags in 500 lb. lots. The slurry was prepared by weighing the hydrate into a measured quantity of water. The slurry was continuously stirred in a 5 gallon vessel equipped with a paddle mixer and a peristaltic recirculating pump. The slurry was filtered to remove sand and coarse particles before feeding to the disk atomizer. Prior to each test the slurry concentration was checked by measuring the specific gravity, and adjusted if necessary. Slurry concentrations reported as "percent" should be read as "percent (wt-vol)". This means, for example, that a 20 percent slurry contains 20g $\text{Ca}(\text{OH})_2$ (wt) for every 100 ml of slurry (vol)

Solid samples were chemically analyzed to determine their calcium and sulfur content. The collected samples were dissolved in hydrochloric acid and oxidized by hydrogen peroxide, followed by neutralization with sodium hydroxide. The resulting liquid was filtered and then diluted to mark in a 100 mL volumetric flask. Aliquots of this solution were then analyzed by [inductively-coupled argon plasma] atomic emission spectroscopy for Ca^{++} and by ion chromatography for SO_4^{--} . The resulting percentage of SO_4^{--} relative to Ca^{++} (after correction for control and blank analyses) is reported as calcium utilization.

The baseline test conditions selected for this study are as follows:

20 percent (wt-vol) $\text{Ca}(\text{OH})_2$ slurry
(20g $\text{Ca}(\text{OH})_2$ /100ml slurry)
100 percent relative humidity (non-evaporating)

Figure 2-2. Drop size distribution for water and 20 percent slurry droplets generated by the rotary disk atomizer.

60°C

100 percent relative humidity (non-evaporating)

20,000 rpm rotor speed

1500 ppm SO₂

Ca/S < 1.0

Sample collection Temperature > 180°C

3.0 EXPERIMENTAL RESULTS

3.1 Baseline Test Results

The data in Figure 3-1 show the slurry utilization vs. time for the baseline reactor operating condition. Sorbent utilization is over 60 percent. Reactivity testing up to this point used bags 2 and 3 from the second 500 lb. shipment from Marblehead Lime Company. Bag 1 from that shipment was used during spray characterization tests with the new SDR design. Variables tested using bags 2 and 3 included slurry concentration and SO_2 concentration.

Figure 3-2 shows the data obtained at the baseline operating condition using bags 2 through 7 from the second 500 lb. shipment of the Marblehead hydrated lime. These data show that utilizations measured for hydrate from bags 4-7 are significantly lower than the 60-65 percent utilizations obtained with bags 2 and 3. Bag 4 had the lowest utilization, about 20 percent. Bags 5 and 6 consistently showed about 23-27 percent utilization, while bag 7 attained 42 percent.

These data are at once striking and revealing. Not only was a wide variation found in reactivity between different bags, but within a single bag of sorbent, measured utilizations were relatively constant, within experimental error, even for tests performed over a month apart. Thus, although the experimental procedure was found capable of producing reliable and reproduceable data, the sorbent supply was highly variable. This point must be kept firmly in mind while reviewing the data in the following sections. Variation must be considered relative to the baseline data for the bag of sorbent employed.

3.2 Sorbent Variability Studies

One of the most significant variables found to impact slurry utilization during this program was the bag of sorbent chosen. Therefore, considerable effort was devoted to determining the critical factor responsible for this variability. Particle size and surface area analyses were conducted early on for bags 2 through 5. The results, shown in Table 3-1, provide no insight.

Figure 3-1. Baseline sorbent utilization measured using Bag 2 of the second shipment of Marblehead calcium hydroxide.

Figure 3-2. Measure calcium utilization for different bags taken from a single 500 lb shipment of Marblehead hydrated lime.

TABLE 3-1. PHYSICAL AND CHEMICAL ANALYSES OF SORBENTS FROM THE SECOND SHIPMENT OF MARBLEHEAD HYDRATED LIME

Bag No.	mm Microns	SSA m ² /g	mol-percent	
			CaCO ₃	Ca(OH) ₂
2	4.0	16.2	-	-
3	4.5	16.6	7.8	92.2
4	2.6	15.6	15.3	84.7
5	3.6	16.6	16.4	83.6
5 (bottom)	-	-	16.9	83.1
6	-	-	25.8	74.2

Subsequently, hydrates from bags 3 through 6 were analyzed gravimetrically to determine their hydroxide and carbonate contents (sufficient sample remaining from bag 2 was not available for this analysis and tests with bag 7 were carried out under a later phase of the program). These data (Table 3-1) show that bag 3 had significantly less carbonate than did the others. The utilizations measured for these sorbents at the baseline reactor condition are plotted in Figure 3-3 as a function of their carbonate contents. The correlation shown in Figure 3-3 is by itself weak because the data cover a very narrow range of carbonate contents. However, a hypothesis proposed to explain these results was shown to be consistent with certain assumptions of the droplet reactivity model.

The hypothesis is that the carbonate occupies the reactive, external surface of the hydrate particles. The carbonate formation need not even have occurred after hydration, although that seems most likely. When the slurry is prepared, the carbonate "blinds" the particles, preventing diffusion of calcium species away from the particle surface. This would shift the dominant resistance to reaction from external to internal diffusion.

An attempt was made to predict this effect using the droplet reactivity model. The approach used was a first-order approximation based upon the limited data. The available surface area of the particles was assumed to correlate linearly with carbonate content, and absence of carbonate implied about $16 \text{ m}^2/\text{g}$ of available hydrate surface area. The results of the model predictions, shown as the curve in Figure 3-3, illustrate that a reasonable prediction of the experimental results can be achieved by making a very simple assumption about the effect of carbonation on the sorbent.

Two further tests were done to test the carbonate blinding hypothesis. The first test involved freshly slaking quicklime to make the slurry. The quicklime was provided by Marblehead Lime Co. and was the from same material used by Marblehead to prepare their commercial hydrate - the baseline test sorbent. A test of the quicklime showed that approximately 10-15 percent of the calcium was in the form of carbonate, approximately the same amount as in bags 4-6 of the baseline hydrate. Thus, this provided a means of determining whether the hydration process would mitigate the deleterious effects of carbonate contamination.

Figure 3-3. Correlation between measured utilization and carbonate content of calcium hydroxides. The curve through the data is a model prediction made assuming that carbonate content correlates with availability of carbonate surface area.

The second test involved recalcining a batch of hydrate from bag 7. The calcination was carried out at 950°C for 6 1/2 hours in an atmosphere of commercial dry nitrogen. Under these conditions all of the CO₂ and hydrate should have been effectively eliminated leaving essentially all calcium oxide. This "carefully calcined" material was then handled and stored in dry nitrogen up to and during the slaking process in order to minimize any possible contact with atmospheric CO₂.

Both of these lime slurries were tested in the SDR at the baseline operating condition. The results of these tests are shown in Figure 3-4 along with the baseline test results for bag 7. The data show that the freshly slaked Marblehead lime achieved utilization comparable with the bag 7 hydrate at the longest sampling distance. This indicates that fresh slaking may provide some advantage in reactivity but does not eliminate the blinding effect of carbonate contamination. Otherwise, utilization in excess of 60 percent would have been expected.

The carefully calcined lime, on the other hand, achieved 52 percent utilization. This lends considerable support to the hypothesis that carbonate contamination is largely or wholly responsible for the variation in reactivity between the different bags of sorbent.

Although the carefully calcined material did not achieve the 62 percent utilization of bags 2 and 3, or the 77 percent predicted by the droplet reactivity model it should be noted that the calcination conditions employed were rather extreme. The reactivity of hydrated lime in furnace dry injection tests has been correlated with both calcination and hydration conditions. The extended time at temperature used here to ensure complete calcination may have sintered, or "dead-burned" some of the lime, reducing its ability to hydrate completely during slaking, and thus availability for SO₂ sorption, though to a lesser extent than carbonate blinding.

3.3 Alternate Sorbents

Two of the three sorbents selected by Gilbert/Commonwealth for demonstration testing under this program were also procured -- Mississippi

Figure 3-4. Utilization of a lime slurry from a "carefully calcined" lime. The carefully calcined lime was prepared at 950°C under a dry nitrogen atmosphere. Data for the baseline Marblehead hydrate and a freshly slaked Marblehead quicklime are shown also.

hydrate and mid-Ohio Valley quicklime. Those were tested as received under the baseline operating conditions. Results of these tests are shown in Figure 3-5. Both sorbents' reactivities lay in the range of data for bags 4-7 of the baseline Marblehead hydrate. The Mississippi hydrate was the most reactive of the two, achieving nearly 34 percent utilization.

3.4 Slurry Concentration Effects

The effect of slurry concentration on sorbent utilization is shown in Figures 3-6 and 3-7. These data were obtained using bag 3 of the Marblehead hydrate. Figure 3-6 shows that the difference in reactivity, from 1 wt-percent to 30 wt-percent slurry is greatest for short sampling distances. At longer distances differences in reactivity diminish, except for the 1 percent slurry which quickly achieves nearly 100 percent utilization. Figure 3-7 shows the same data set, but this time represented as utilization vs. slurry concentration. In Figure 3-7 it is more apparent that slurry concentration has a dramatic effect on utilization only for concentrations below 5 wt-percent.

3.5 Droplet Diameter

Droplet mean diameter was increased by reducing the atomizer speed to 10,000 rpm. Referring back to Figure 2-2, this gives a mass median diameter of 69 μm with 80 percent of the mass between 10 and 90 μm . Figure 3-8 shows the measured sorbent utilization under this condition. Overall, the data lie within the range of the baseline test results obtained using bag 4 of the Marblehead hydrate. However, the data trend is flatter than generally observed. Model predictions concur that under non-evaporating conditions drop size should have a small effect in the range examined here.

3.6 SO₂ Concentration

The data in Figure 3-9 show the increase in slurry utilization with increasing sampling distance (from the reactor entrance) at 100, 500, and 1500 ppm SO₂. These data were obtained using bags 2 and 3. No increase in utilization is observed beyond 17 cm regardless of SO₂ concentration. The same

Figure 3-5. Comparison of alternative sorbents reactivity under baseline test conditions.

Figure 3-6. Effect of slurry concentrations on sorbent utilization at baseline test conditions of 60°C, 1500 ppm SO₂, 20 kpm atomizer speed. Data obtained with bag 2.

Figure 3-7. Slurry concentration dependence of sorbent utilization at baseline test condition of 60°C, 1500 ppm SO₂, 20 krpm atomizer speed. Data obtained with bag 2.

Figure 3-8. Impact of drop size on slurry reactivity. Triangles are data for 70 μ m mmnd droplets. Data obtained using bag 4.

Figure 3-9. Sorbent utilization measured at 100, 500, and 1500 ppm SO₂.
Data obtained using bags 2 and 3.

data are plotted in Figure 3-10 to show the impact of SO_2 concentration on slurry utilization. For these test conditions SO_2 concentration has an effect on utilization for concentrations as high as 1500 ppm.

Figure 3-11 shows the effect of higher (than the baseline) SO_2 concentration on measured slurry utilization. The results shown were obtained with bag 4. These data imply that higher SO_2 concentrations give faster sulfation rate only at short times. This is consistent with a model which assumes external mass transfer control at longer times. However, the measured increase in utilization is not proportional to the increase in SO_2 concentration. The data shown in Figures 3-9 and 3-10 suggested that at SO_2 concentrations below 1500 ppm, a roughly proportional effect was obtained.

3.7 Impact of Sorbent Surface Area

In addition to the baseline calcium hydroxide sorbent, which has an average surface area of $15 \text{ m}^2/\text{g}$, a high surface area hydrate was prepared using an alcohol hydration procedure. In this procedure methanol is added to the hydration water. The added material reduces the stability of calcium ions, thereby slowing the rate of hydration. This prevents localized over heating which presumably "burns" the lime and reduces hydrate reactivity. It also moderates the reaction temperature by boiling off and carrying away excess heat.

Figure 3-12 shows that the high surface area material actually achieves a moderate utilization which is higher than all but bags 2 and 3 of the Marblehead hydrate. This suggests that the surface area of the starting material is not the most critical factor in determining reactivity. It also implies that other differences between materials can greatly affect sorbent utilizations. The mean particle diameter of the alcohol hydrate was $1.2 \text{ }\mu\text{m}$, somewhat smaller than the Marblehead hydrate (see Table 3-1).

A "cation scan" was performed on representative samples of the alcohol hydrate, and samples from bags 2 and 3. The results for bags 2 and 3 were essentially similar and were averaged. These results are shown in Table 3-2. Unfortunately, these results indicate nothing of particular significance. Most of the cations detected are present at only trace quantities and never differ by

Figure 3-10. Impact of SO₂ concentration on measured sorbent utilization at different sampling distances. Data obtained using bags 2 and 3.

Figure 3-11. Impact of high SO₂ concentration on slurry utilization with Bag 4 of the Marblehead AHL

Figure 3-12. Difference in reactivity between a commercial hydrated lime (Marblehead, 15 m²/g) and an in-house prepared high surface area hydrated lime (50 m²/g). Experiments were carried out at baseline test conditions.

TABLE 3-2. CHEMICAL ANALYSIS OF MARBLEHEAD AH (COMMERCIAL)
AND ALCOHOL HYDRATE (PREPARED IN-HOUSE)

Element	<u>Concentration (mg/g)</u>		<u>Ratio</u>
	Marblehead AH	Alcohol Hydrate	Normalized to Calcium
Al	1.3989	1.2248	1.1247
Sb	-----	-----	-----
As	-----	-----	-----
Ba	0.0152	0.0296	2.5014
Be	-----	-----	-----
B	-----	0.0119	-----
Cd	-----	-----	-----
Ca	532.9	414.9	*0.7786
Cr	0.0019	0.0040	2.7039
Co	-----	-----	-----
Cu	0.0057	0.0059	1.3294
Au	-----	-----	-----
Fe	2.2840	1.9755	1.1109
Pb	-----	-----	-----
Mg	5.5196	9.6800	2.2524
Mn	0.1427	0.3161	2.8450
Hg	-----	-----	-----
Mo	-----	-----	-----
Ni	-----	-----	-----
K	-----	0.3951	-----
Se	-----	-----	-----
Si	3.8066	3.5559	1.1998
Ag	-----	-----	-----
Na	0.2665	0.2173	1.0472
Sr	0.2474	0.0869	0.4511
Tl	-----	-----	-----
Sn	0.0295	0.0573	2.4947
Ti	0.0466	0.0395	1.0887
V	0.0038	0.0079	2.6701
Zn	0.0086	0.0099	1.4785
insolubles	27.56	26.23	1.2226

*This value represents the actual ratio of the calcium concentrations
in the two sorbents

more than a factor-of-three between the two materials. Only the calcium concentrations are significantly different between the two materials.

One hypothesis which was tested in an attempt to explain these data is that residual methanol from the hydration process may have in some way reduced the calcium solubility, thereby shifting the reaction to internal mass transfer control. The amount of residual methanol in the lime could not easily be determined. However, in order to test this hypothesis slurries were prepared using water containing 1.25% v/v and 4.75% v/v methanol. These concentrations were selected simply as convenient. By using two concentrations differing by about a factor of four it was hoped that any effect would readily be exposed. Results of these tests (using bag #5) are shown along with the baseline test results in Figure 3-13.

The results in Figure 3-13 lie within the range of data for the baseline condition (broken curve). Interestingly, the utilization measured for the lower methanol concentration were the lower. The appearance of the data, however, (the curves are essentially parallel) suggests that this is most likely due to a systematic bias in the chemical analysis.

3.8 Effect of CO₂ on Slurry Reactivity

Figure 3-14 shows that eliminating CO₂ from the reactor atmosphere had no noticeable effect on the slurry reactivity. The tests were done by generating a hydrogen flame with 100 percent excess theoretical air. This provided the necessary 60°C dewpoint. All other experimental conditions were the same as the baseline. Although the data in Figure 3-14 tend to lie above the baseline curve, they are well within the normal data spread observed using bags 4 - 6.

3.9 Droplet Evaporation

Figure 3-15 illustrates the results of tests performed in an evaporating mode, where the relative humidity of the reactor was near zero percent. Model predictions (curves) are also shown. The data show that the short time reactivity is similar for evaporating and non-evaporating conditions, but the

Figure 3-13. Utilization of Marblehead AH slurries containing 1.25% and 4.75% v/v methanol. Tests with methanol and baseline curve shown were obtained using bag 5.

Figure 3-14. Impact of CO₂ on baseline sorbent utilization using bag 4.

Figure 3-15. Data and model predictions for evaporating and non-evaporating cases. All data obtained using bag 2. Non-evaporating data were obtained at the baseline condition. Evaporating data were obtained with only ambient moisture levels (approx. 90°C approach to saturation).

reaction is halted under evaporating conditions when the slurry droplet becomes dry.

The model predicts that the rate of SO_2 uptake by an evaporating droplet should be greater than that of a non-evaporating droplet. This results from the accumulation of sorbent at the droplet surface during evaporation. When this occurs an excess of calcium is present at the droplet surface and the minimal diffusional distances for both the calcium and sulfur species results in a rate of SO_2 absorption approaching the limit of external mass transfer. A non-evaporating droplet, by contrast, has relatively long diffusional distances which increase with time as the sorbent near the surface is consumed. The rate of SO_2 uptake is then limited by liquid phase mass transfer (short times only). In contrast to the above discussion, the data shows utilization to be lower for the evaporating case. This is likely a result of the high approach to saturation used during the evaporating case (90°C throughout the length of the reactor) which caused an evaporation rate greater than that which would normally be encountered in a duct.

3.10 Enhancement Strategies

The data presented thus far coupled with the brief discussions of the droplet reactivity model should give the impression that the maximum attainable slurry utilization will not be limited by the droplet characteristics, but, rather, by the rate of diffusion of SO_2 to the droplet surface. This would leave little room for enhancement strategy directed at the slurry properties. However, as the data have shown, slurries prepared from commercial limes and hydrates may not be able to achieve their potential utilization due to carbonate blinding, poor calcination or hydration conditions, or other factors not yet identified. Thus, potential enhancement strategies were investigated with regard for their ability to maintain slurry droplet reactivity at or near the limit of external mass transfer control.

The investigation of enhancement strategy was conducted using bag 7 of the Marblehead hydrate. That bag of sorbent achieved 42 percent utilization at the baseline operating condition. Three approaches to slurry reactivity enhancement were addressed. The first was to try to increase the calcium ion solubility by

the addition of the soluble anions formate and acetate. The second was to increase the SO_2 solubility and mobility by the addition of sodium ion to the slurry. The third approach was the addition of sodium salts to determine whether a synergism would take place between the first two approaches.

Acetic and Formic acids were used to provide the soluble anions in hopes of increasing the calcium solubility. A rough check of the slurry pH was made before and after addition of the acids. Within the resolution of the indicating paper used, the pH remained constant at about 13 although 10 mol-percent of acid relative to calcium was used in each case.

With little or no change in pH (which was anticipated) only a slight change in calcium solubility was expected. However, during the addition of the acids an effervescence of the slurry was evident at the point of acid mixing. This was undoubtedly due to a temporary local drop in pH and subsequent decomposition of calcium carbonate. Hence, it is possible that the addition of the acids may have partially reduced the effects of carbonate blinding.

Results of the acid addition tests are shown in Figure 3-16. The data indicate that formic acid addition significantly enhanced the sorbent performance, achieving 47 percent utilization at the longest sampling distance. Results from the acetic acid addition are less clear, however. At the 33 cm sampling location a 5 percent utilization increase is observed but overall the results seem to be within the range of the baseline data.

Sodium hydroxide, and the formate, acetate, and chloride salts of sodium were each added to slurries produced from bag 7 of the Marblehead hydrate at 10 mol-percent relative to calcium. Results for each of these tests at the baseline reactor condition are shown in Figure 3-17. These data show that all of the sodium compounds produced significant increases in sorbent utilization. The increase in utilization was in each case several times greater than the stoichiometric increase attributable to the sodium. A notable point about these data is that the results achieved for the chloride, acetate, and formate were nearly identical to those for the hydroxide.

Figure 3-17. Impact of sodium hydroxide and sodium salts on the measured utilization of Marblehead hydrate taken from bag 7. The additives were present at 10 mol percent relative to calcium.

Data quality remained a critical issue throughout this experimental program. Especially key in this area are the incumbent problems of sampling a reactive solid from a gas mixture. This was addressed by minimizing the sample collection time and by flash drying the slurry, rendering it relatively unreactive, during sample collection. In order to continuously monitor the efficacy of these precautions "background" and "probe capture" tests were run at each test condition.

Sample collection times were limited to 5 minutes, except for the 1- and 2-percent slurry concentrations, for which 15 minute samples were obtained. Probe capture tests, however, all ran for 15 minutes. In the probe capture test a sample of slurry was collected, SO_2 was then introduced to the reactor and drawn through the sampling system to expose the fresh dried sorbent.

Probe capture utilizations typically varied from 0.1% to 9% over the course of the program. Some results from bag 2 are shown in Table 4-1. The measured probe capture utilizations are considered to represent upper limits for two reasons. First of all, the sample exposure time in the filter holder is six times the average exposure time of a sorbent particle during sampling. Secondly, sorbent reactivity is much greater for fresh sorbent than it is already reacted material.

In support of the model development task two special probe capture tests were run. In the first, SO_2 was introduced to the reactor by a tube placed adjacent to the sampling probe entrance. This restricted the slurry reaction to the hot, evaporating environment inside of the probe. The second test involved measuring in-probe SO_2 capture while water spray was introduced to the reactor. The objective was to determine the effect of "wetting" the probe filter by the occasional unevaporated droplet.

Results of these tests are shown in Figure 4-1 alongside the baseline SO_2 capture at 17 cm (bag 4) and the average measured probe capture. Results of the first test indicate that even fresh unreacted slurry will not capture very much SO_2 in the brief (<30 ms) evaporating zone inside the probe. The total measured

TABLE 4-1. MEASURED IN-PROBE SO₂ CAPTURE (15 MINUTE EXPOSURE 1500 PPM SO₂)
USING THE OIL-HEATED SAMPLING PROBE

<u>Sample No.</u>	<u>Sample Temperature</u>	<u>Utilization Percent</u>
127712	135	3.3
127704	127	4.8
127680	157	0.75

Baseline SO₂ Capture:

- Normal test. Sample collection at 17 cm

"Normal" Probe Capture:

- Sample collected in absence of SO₂. Then exposed to SO₂, on filter, for 15 minutes.

In-Probe-Only SO₂ Capture:

- SO₂ is introduced at probe entrance while sample is collected

Probe Capture w/H₂O:

- Same as "Normal" probe capture, but water spray is added to reactor during SO₂ exposure

Figure 4-1. In-probe SO₂ capture test results compared with baseline.

utilization is roughly twice that of a normal probe capture test. The second special test shows that water spray has little impact on measured "on-filter" probe capture. Visual inspection of the sample revealed a smooth, glassy surface, demonstrating that unevaporated droplets did reach the filter. However, the measured utilization is merely on the high side of the range of normal probe capture results.

Data collected in the experimental phase of this program indicate that lime slurry utilization is most sensitive to the gas-phase SO_2 concentration and to the slurry concentration. The effects of initial sorbent surface area and slurry droplet diameter were unclear. Gas-phase CO_2 had no effect on slurry utilization in these experiments. Slurry utilization was not improved at short times by allowing the droplets to evaporate. Further, overall utilization was best under saturated conditions.

A key parameter found in these tests is the material used to prepare the slurry. Some variation was found between hydrates from different sources, and it was shown that fresh-slaked lime can be more reactive than slurry prepared from hydrate. However, the most significant discovery was the range of utilizations obtained from different bags of material from the same source. At the baseline test condition slurry utilizations for Marblehead AH were found to vary from about 19% to about 65%. The only explanation found to consistently account for this is carbonation of the sorbent, resulting in reduced calcium availability, and a shift from external to internal mass transfer control of the reaction rate.

The addition of several promoters helped to alleviate the deteriorated performance of the hydrates. Acetic acid caused about 5 percent utilization increase for slurry prepared from bag 7 while formic acid effected over 10 percent increase at the longest sampling distance. Sodium salts and sodium hydroxide produced even greater increases in utilization. Sodium salts added to a 20 wt-percent lime slurry increased the measured utilization from about 42 percent to as high as 63 percent. However, this is still no greater than the utilization measured for the most reactive un-promoted hydrate tested.

PART II IN-DUCT SLURRY DROPLET PROCESS MODEL

6.0 INTRODUCTION

Duct injection of calcium based sorbents offers a potential low cost strategy for SO_2 control from existing coal fired boilers. The economics of the process are, however, almost completely dominated by sorbent costs since this is a low capital but high operating cost process. The key to achieving overall cost effectiveness is therefore to maximize sorbent utilization. To do this the fundamental processes which limit sorbent utilization must be understood. The low temperature capture of SO_2 by calcium based sorbents is a complicated process which may occur simultaneously with the evaporation, humidification, condensation, and moisture adsorption processes. Prediction of SO_2 capture in a duct is difficult as the process is controlled by mechanisms which are not necessarily obvious.

The development of a sophisticated model of the sulfation processes which accounts for the many sub-processes which would occur in a duct serves two purposes. First, such a model provides a valuable guide in the planning of fundamental and pilot scale experiments designed to determine the mechanisms which control in-duct SO_2 capture. Second, once such a model has been developed and validated against experimental data, it may be used as a tool in designing in-duct flue gas desulfurization systems.

The model developed under this program is a one-dimensional model which considers the simultaneous humidification and SO_2 removal processes. The model considers the three types of injection strategies being considered for use on full scale processes:

- Injection of a slurry directly into the duct;
- Injection of dry sorbent followed by injection of a water spray; and
- Injection of a water spray followed by injection of dry sorbent.

A submodel which considers the scavenging of sorbent by inertial impaction is required for the second injection strategy. This report describes the fundamental basis of this model and its operation.

The model is a fully coupled one-dimensional model of the simultaneous humidification and SO_2 removal processes. The model considers a size distribution of drops sprayed into a duct where the resulting drops decelerate to the gas velocity and, while decelerating, may scavenge particles suspended in the gas phase. The solid reactant, calcium hydroxide, may be injected as a slurry or as a dry particle which may either be subsequently scavenged by the spray or, if the duct has been pre-humidified, form a condensate and subsequently react with SO_2 .

7.1

Slurry Droplet Model

The slurry droplet model handles both the slurry injection strategy and the scavenging injection strategy. A total of nine differential equations governing drop deceleration, drop temperature, drop evaporation, gas temperature, particle scavenging, particle diffusion within the droplet, liquid phase SO_2 diffusion, liquid phase diffusion of calcium in the bulk liquid phase, and sorbent utilization are solved simultaneously for an input drop size distribution. The reaction of sorbent with sulfur scavenged by a spray is considered in the same manner as sorbent within a slurry drop. When evaporation is complete the reaction of SO_2 with the dried agglomerate is considered.

The SO_2 reactivity model contains an extensive description of the SO_2 -slurry droplet reaction. The model accounts for:

- Diffusion of SO_2 from the bulk gas phase to the droplet surface;
- Equilibrium absorption of SO_2 at the droplet surface;
- Instantaneous dissolution of SO_2 to H_2SO_3 ;
- Equilibrium ionization of H_2SO_3 to HSO_3^- ;
- Liquid phase diffusion of H_2SO_3 and HSO_3^- from the droplet surface to the droplet interior;

- Dissolution of Ca(OH)_2 at the sorbent surface; and
- Diffusion of Ca(OH)_2 from the sorbent surface to the bulk liquid phase.
- Liquid phase diffusion of H_2SO_3 and HSO_3^- from the bulk liquid phase to the sorbent particles;
- Diffusion of Ca(OH)_2 from the droplet interior (where SO_2 does penetrate) outward;
- The influence of the bulk flow of water outward through the accumulated sorbent particles at the droplet surface on the diffusion of both calcium and sulfur species;
- The influence of recycle on SO_2 capture and internal processes; and
- The presence of ash scavenged by the spray and present in the recycle.

Work by Constan and Calvert (1963) suggests that internal circulation within slurry droplets is not significant. The model therefore assumes that sorbent particles are initially uniformly distributed throughout the droplet and that they do not circulate within the droplet. As water evaporates from the droplet, the droplet surface recedes and encounters particles which were initially near the droplet surface. As evaporation continues, the receding surface pushes these particles inward and an accumulation of sorbent particles at the droplet surface occurs. This is illustrated in Figure 7-1. Harriott (1962) determined that irregularly shaped particles typically have a packing density of 0.5 - 0.6. The model assumes that the sorbent particles have a packing density of 0.6. A particle concentration gradient is created between those crowded together at the surface and those within the droplet which still have the droplet's initial particle concentration. Although sorbent particles will therefore diffuse inward, the rate of this diffusion is relatively slow.

Figure 7-1. Illustration of the accumulation of sorbent and product at the droplet surface as evaporation shrinks the surface.

Figure 7-2. The two types of reaction fronts.

The instantaneous liquid phase reaction between the sulfur and calcium species can occur at two types of reaction fronts within a slurry droplet (illustrated in Figure 7-2). As the liquid phase sulfur species diffuse into the droplet they pass sorbent particles which are simultaneously diffusing calcium outward. According to film theory, calcium which has dissolved at the surface of a sorbent particle will diffuse outward through a film whose thickness can be calculated. (When sorbent particles are far apart the film thickness will equal that for a particle in an infinitely dilute solution. If the particles are packed together, the film thickness will be reduced.) A calcium/sulfur reaction front will therefore be present at the outer edge of this film. The sulfur species in the surrounding bulk liquid phase will, however, also diffuse inward. The distance that calcium must diffuse outward will therefore be less than that calculated by film theory and, since the rate of sulfur diffusion inward is dependent on the bulk liquid phase concentration of sulfur species, the distance of the reaction front from the surface of a sorbent particle will vary depending on the local concentration of liquid phase sulfur species.

Calculations of the film thickness when sulfur is present indicate that the reaction between calcium and sulfur species occurs in the liquid phase. It is therefore assumed that the product of the calcium/sulfur reaction ($\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}$) precipitates out either as separate crystals or on the surface of ash particles which were scavenged when the droplets were sprayed into the duct at high velocities. Calcium sulfite in the droplet is located in the radial shell where the reaction occurs (either in the shell where the reaction is occurring around the individual sorbent particles or in the radial shell where the bulk reaction is occurring).

Since the liquid phase reaction is assumed to be instantaneous, the concentration of sulfur species may drop to zero at some radial position within the slurry droplet. If this occurs, dissolved calcium at the center of the droplet will diffuse outward to this radial position and the second type of reaction front will develop at that radial location.

The accumulation of sorbent particles at the droplet surface will have three effects on the sulfur uptake processes. First, the high solid to liquid volume ratio will hinder liquid phase diffusion of calcium and sulfur species.

Second, the closeness of sorbent particles to each other will reduce the film thickness around these particles which will have the effect of increasing the reactivity of a sorbent particle. Third, the evaporation of water at the outer surface of the accumulated sorbent particles will require that a bulk flow of water pass through this layer. This bulk flow of water will increase the rate of calcium diffusion outward and hinder the diffusion of sulfur species inward.

7.1.1 Single Drop Evaporation

The rate of droplet evaporation will be governed by the simultaneous mass and heat transfer processes between the droplet and surrounding gases. When the effect of water evaporation is taken into account, the rates of mass (N_w) and heat (Q) transfer may be given as:

$$N_w = K_w \pi D_d^2 C_f \ln \frac{1 - x_{ds}}{1 - x_e} \quad (1)$$

$$Q = h \pi D^2 (T_g - T_d) \left(\frac{\theta}{e^\theta - 1} \right), \quad (2)$$

$$\text{where } \theta = \frac{9 N_w C_p}{\pi k D}.$$

By definition, the amount of water contained in a drop will decrease by:

$$dm_w/dt = -N_w M_w. \quad (3)$$

Changes in drop temperature will be a function of heat transfer to the drop, heat lost due to evaporation, and the heat of reaction resulting from the calcium/sulfur:

$$\frac{dT_d}{dx} = \frac{6}{C_p D^3 \rho} \left[\frac{(Q - N_w)}{\pi V} + \frac{n D_p (1 - \epsilon) \Delta H_R}{2 V'} \frac{dd_p}{dx} \right] \quad (4)$$

The presence of dissolved solids in the droplet will influence the vapor pressure of water at the droplet surface and thus the evaporation rate. The vapor pressure of water with dissolved CaCl_2 is given by:

$$P_w = a * \text{EXP}(18.3036 - 3816.44/(T_d - 46.13))$$

were the vapor pressure of water is in mm Hg. From Kinzey (1988), the activity of water is given by:

$$a = .9899 - 8.678E-3X_m - 3.676E-2X_m^2 + 4.624E-3X_m^3 - 1.667E-4X_m^4.$$

When the droplet dries to the point where the sorbent particles touch and the water recedes into the droplet, evaporating water must diffuse out of the porous agglomerate. Flux through the porous agglomerate can be derived from Kinzey (1988) as:

$$N_w = B(x' - x_{sat}) \quad (5)$$

where:

$$B = \frac{D_{w,eff} c_{q,d}}{(r_s/r_c)(r_c - r_s)} \quad (6)$$

The effective diffusivity of water through the porous agglomerate is calculated from:

$$D_{w,eff} = D_w(1 - V_{close\ packing}).$$

The flux in Eqn. 5 can be equated to external mass transfer to obtain the overall rate of evaporation:

$$N_w = B[(Bx_{sat} - k_{m,w}x_w)/(B - k_{m,w}) - x_{sat}] \quad (7)$$

The presence of dissolved solids will prevent the complete evaporation of water and thus result in an equilibrium amount of water present in the agglomerate after evaporation has ceased.

7.1.2 Gas Phase Temperature

Cooling of the duct gases results from heat transferred to the drops, Q , and heat required to heat the evaporating water from the drop temperature to the local duct temperature. Overall cooling of the ducts gases is determined by integrating over the distribution of drop sizes:

$$\frac{dT_g}{dy} = - \frac{1}{C_{p,g} F_g} \int_i \frac{1}{V_d} [N_{w,i} C_{p,wv} (T_g - T_{d,i}) + Q_i] df_i \quad (8)$$

7.1.3 Particle Scavenging

Scavenging of particles larger than 0.5 microns will occur by inertial impaction and interception. Scavenging due to impaction is given by:

$$N_I = \frac{N_{IV} + N_{IP} \text{ Re}/60}{1 + \text{Re}/60}$$

where:

$$N_{IV} = \frac{1}{\left[1 + \frac{0.75 \ln(4\psi)}{2\psi - 1.214} \right]^2},$$

$$N_{IP} = 4\psi^2 / (2\psi + 0.5)^2, \text{ and}$$

$$\psi = \frac{\rho_p d_p^2 (V_d - V_p)}{18\mu D}$$

Scavenging by interception is calculated by:

$$N_{IC} = \frac{N_{cv} + N_{cp} \text{ Re}/60}{1 + \text{Re}/60}$$

where:

$$N_{cv} = (1 + d_p/D)^2 - \frac{3}{2}(1 + d_p/D) + \frac{1}{2(1 + d_p/D)}, \text{ and}$$

$$N_{cp} = (1 + d_p/D)^2 - 1/(1 + d_p/D).$$

Scavenging due to both mechanisms is given by:

$$N_T = 1 - (1 - N_I) (1 - N_{IC}).$$

Assuming that the drops are evenly distributed across the duct allows the development of a rate equation governing the number of particles captures by a drop:

$$\frac{dn}{dy} = \frac{3D^2 F_s N_T}{2d_p^3 \rho_p V_p V_d} (V_d - V_p) \quad (9)$$

Local overall scavenging in the duct is found by integrating over the drop size distribution. (Note: when a slurry is injected and there is no scavenging occurring, n is calculated initially and this equation is not solved.)

7.1.4 Drop Deceleration

A drop injected at a high velocity into a duct will decelerate primarily due to drag forces between the drop and surrounding gases. When scavenging of solids from the gas stream is significant the loss in momentum due to these collisions must be allowed for. The rate of drop deceleration can then be written as the sum of these two effects (note that the term dV_g/dx has been assumed negligible),

$$\frac{d(V_d - V_g)}{dy} = - \frac{3\rho_2 C_d}{4\rho_p D V_d} (V_d - V_g)^2 - \frac{\pi d_p \rho_p}{6} (V_d - V_g) \frac{dn}{dy} \quad (10)$$

where, for an evaporating drop, the drag coefficient is given by Ingebo (1956) as:

$$C_d = \frac{27}{Re^{0.84}}$$

When the spray direction is not horizontal the effect of gravity may also be taken into account.

7.1.5 Particle Diffusion

Kinzey (1988) evaluated the importance of circulation within a 50 μm spherical droplet falling at its terminal velocity on liquid phase diffusivity and found only a minimal increase in the effective diffusivity. This finding can be extended to the diffusivity of sorbent particles within a slurry droplet. The model therefore assumes that, except for the short period during which the droplet is decelerating, the position of sorbent particles will only change due to diffusion.

The model assumes that sorbent particles are initially uniformly distributed throughout the droplet. (In the case where the sorbent particles are scavenged from the gas phase, it is assumed that the high degree of external turbulence during droplet deceleration results in mixing within the droplet that is sufficient to ensure a uniform distribution.) As water evaporates from the droplet, the droplet surface recedes and encounters particles which were initially near the droplet surface. As evaporation continues, the receding surface pushes these particles inward and an accumulation of sorbent particles at the droplet surface occurs. A particle concentration gradient is created between those crowded together at the surface and those within the droplet which still have the droplet's initial particle concentration. The sorbent particles will therefore diffuse inward. The rate of diffusion of these particles is calculated by:

$$\frac{dc_n}{dt} = -4\pi R^2 D_p \frac{dc_n}{dR} \quad (11)$$

where D_p is given by the Stokes-Einstein equation:

$$D_p = k_b T_d / 3\pi\mu d_p$$

7.1.6 Reaction of Sulfur Species with Sorbent Particles in Slurry Drop

The reaction between calcium hydroxide and SO_2 in the liquid phase is assumed to be instantaneous. The rate of calcium utilization will therefore depend on the rate calcium hydroxide molecules leave the sorbent surface and the

rate of diffusion from the surface to the bulk liquid phase where the reaction occurs. The distance that the calcium (hydroxide) diffuses will be a function of how close the neighboring sorbent particles are. If they are far away this distance will equal the distance which can be calculated for a particle in an infinite medium (via a Sherwood Number). If the sorbent particles are close this distance can be calculated as:

$$\delta' = \frac{d_p}{2} \left[\frac{1}{(1-w)^{1/3}} - 1 \right] \quad (12)$$

When liquid phase sulfur species are present in the bulk liquid phase around the sorbent particle, the liquid phase species will also diffuse inward, thus decreasing the distance $\text{Ca}(\text{OH})_2$ must diffuse outward. Calcium will therefore be diffusing outward to a reaction front which surrounds the sorbent particle and sulfur species will be diffusing inward. By the pseudo-steady state assumption, the flux of calcium dissolution at the sorbent surface, the flux of calcium hydroxide diffusion outward from the sorbent particle, and the flux of H_2SO_3 and HSO_3^- inward to the sorbent particle will be equal and can be given in terms of spherical coordinates as:

$$d_p^2 \sigma k_d (c_{L,e} - c_L^*) = \frac{4D_L (c_L^* - c_L)}{[2/d_p - 1/(d_p/2 + \delta)]} = \frac{4(D_1 c + D_2 c^2/K_d)}{[1/(d_p/2 + \delta) - 1/(d_p/2 + \delta')]} \quad (13)$$

where δ is the distance from the particle surface to the reaction front. The roughness factor, σ , accounts for the loss in surface area as the reaction proceeds. Since this factor is dependent on the unknown structure of a sorbent particle, an empirical factor must be used:

$$\sigma = A/A_s = 1 + \exp[a(d_p/d_{p,o})^3 - b]$$

If it is assumed that σ equals 2 when 20% of the particle has been utilized, than:

$$b = -0.8a;$$

where a is calculated from the surface area of the sorbent. The diffusivity of lime, D_L , is calculated from theory as:

$$D_L = 3.954 \times 10^{-9} T_d e^{(-2046/T_d)} \text{ (m}^2/\text{s)}.$$

Since the liquid phase reaction is assumed to be instantaneous, the bulk liquid phase concentration of lime, c_L , can be set equal to zero and the equations given by (13) can be solved for the concentration of calcium at the particle surface, c_L^* :

$$c_L^* = \frac{c_{L,e}}{1 + \frac{4D_L}{\left[\sigma k_d d_p^2 \right] \left[\frac{2}{d_p} - \frac{1}{(d_p/2 + \delta)} \right]}}; \quad (14)$$

and the distance from the particle surface to the reaction front;

$$\delta = \frac{c_{L,e} \delta' + (D_1 c + D_2 c^2 / K_d) (1 + 2\delta' / d_p) / \sigma k_d}{c_{L,e} + (D_1 c + D_2 c^2 / K_d) (1 + 2\delta' / d_p) (1/D_L + 2/d_o \sigma k_d)} \quad (15)$$

The rate of utilization of a sorbent particle is then:

$$\frac{dN_{Ca}}{dt} = \frac{\pi(c_{L,e} - c_L)}{\frac{1}{d_p^2 \sigma k_d} + \frac{2/d_p - 1/(d_p + \delta)}{4D_L}}; \quad (16)$$

where c_L equals zero when liquid phase sulfur species are present.

7.1.7 Reaction of Sorbent in Wet Agglomerate

Once the slurry drop has dried SO_2 will continue to react with the resulting moist agglomerate of sorbent particles. The rate of sorbent utilization is calculated by the grain model:

$$\frac{dN_{Ca}}{dt} = \frac{\pi d_p^2 c_s}{\left[\frac{1}{\sigma k_r} + \frac{d_c}{D_s} \left[1 - \frac{d_c}{d_p} \right] \right]}. \quad (17)$$

7.1.8 Reaction of Scavenged Sorbent During Deceleration

When water is sprayed into a duct at high velocities it will scavenge sorbent already suspended in the duct by inertial and interception mechanisms. During this period when the droplets are moving at a high velocity there will be some circulation for sorbent particles within the drop. The rate of utilization of these particles is calculated with Eq. 16. The film thickness (δ) is found by equating the rate of external mass and the sum of the rate of sorbent utilization for all particles within the drop:

$$[k_m Y_w + Y_{ds}(N_w - k_m)] = \frac{n d_p^2 (c_{L,e} - c_L)}{(\delta/2D_L + 1/\sigma k_d)} \quad (18)$$

There are two unknowns in this equation: the gas phase concentration of SO_2 at the droplet surface, Y_{ds} , and the film thickness, δ . Although the film thickness can be calculated by Eq. 15, Eq. 15 requires the liquid phase sulfur concentration which is a function of Y_{ds} via Henry's constant. If δ' (Eq. 12) is calculated by assuming a Sherwood Number of 2 and Eq. 18 is solved for Y_{ds} as a function of δ , a simple iterative solution is sufficient. This involves guessing an initial Y_{ds} , calculating δ by Eq. 15, recalculate Y_{ds} by Eq. 18, and resubstituting the new Y_{ds} in Eq. 15 until the value of the film thickness converges.

7.1.9 Liquid Phase Diffusion of Sulfur Species

When SO_2 is absorbed at the droplet surface, water and SO_2 react to form H_2SO_3 which then dissociates into HSO_3^- and SO_3^{--} . It is assumed in the model that these steps are rapid and have reached equilibrium. The presence of SO_3^{--} is ignored since its concentration is several orders of magnitude less than that of HSO_3^- . The concentration of dissolved SO_2 can be calculated by Henry's law. The results of Rabe and Harris (1963) can be rewritten to give a Henry's constant of:

$$H_e = \text{EXP}(2.4717 - 2851.1/T_d)$$

where H_e is in atmospheres/mole fraction dissolved SO_2 (as SO_2 , H_2SO_3 , HSO_3^-) and T_d is the temperature in degrees Kelvin.

Once SO_2 is absorbed, it will react with H_2O to form H_2SO_3 which will dissociate to HSO_3^- and SO_3^{--} . The concentration of SO_3^{--} is negligible and can be ignored. Since both H_2SO_3 and HSO_3^- will diffuse into the droplet interior, both their concentrations must be known. Kinzey (1988) gives the concentration of HSO_3^- in terms of the dissociation constant and H_2SO_3 :

$$c_1 = (K_d c_2)^{-.5} \quad (19)$$

where the dissociation constant (mol/m^3) is given by :

$$K_d = \exp(22.426 - 1775/T_d - .045T_d).$$

The liquid phase diffusivities of H_2SO_3 and HSO_3^- are given by Kinzey (1988) as:

$$D_2 = T_d \exp(-19.895 - 1800/T_d)$$

$$D_1 = 1.7856 \times 10^{-13} T_d / (1/(4.86T_d - 1100) + 1/(1.46T_d - 390))$$

The diffusion of the these two sulfur species will then be governed by the partial differential equation:

$$\frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 D_1 \frac{\partial c_1}{\partial R} + R^2 D_2 \frac{\partial c_2}{\partial R} - R^2 N_w \left[\frac{(c_1 + c_2)}{c_d} \right] \right] = \frac{(\pi d_p^2 c_{L,e} e_p)/(1 - V_s)}{\frac{1}{d_p^2 \sigma k_d} + \frac{2/d_p - 1/(d_p + \delta)}{4D_L}} \quad (20)$$

The evaporation rate, given by N_w , will have a value of zero in Eq. 20 except when a layer of sorbent particles has accumulated at the droplet surface when it will equal the evaporation rate at the droplet surface. Substitution of Eq. 19 allows this equation to be written for c_1 . The first boundary condition of Eq. 20 states that at the drop surface, the flux of external mass transfer must equal the flux of liquid phase sulfur species. The second boundary condition will depend on the rate at which calcium can dissolve and diffuse from the sorbent particles. If it is relatively slow, symmetry requires that:

$$dc_1/dR = 0$$

at the center of the drop. If it is fast, however, the concentration of liquid phase sulfur species may drop to zero at some radial location where a reaction front between calcium hydroxide diffusing outward and sulfur species diffusing inward develops. The flux of calcium hydroxide outward must equal the flux of sulfur diffusing inward at this reaction front and the boundary condition is given by:

$$D_1 \frac{\partial c_1}{\partial R} = -D_L \frac{\partial c_L}{\partial R}$$

The evaporation terms and the $\partial c_2/\partial R$ term drop out since c_1 is zero at the reaction front.

7.1.10 Liquid Phase Diffusion of Calcium Hydroxide

When the liquid sulfur species do not penetrate to the center of the droplet, calcium hydroxide will dissolve and diffuse outward to a reaction front. Diffusion of calcium hydroxide will be governed by:

$$\frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 D_L \frac{\partial c_L}{\partial R} + R^2 N_w \frac{c_L}{c_d} \right] = \frac{[\pi d_p^2 e_p (c_{L,e} - c_L)]/[1 - V_s]}{\frac{1}{d_p^2 \sigma k_d} + \frac{2/d_p - 1/(d_p + \delta)}{4D_L}} \quad (21)$$

Again, the evaporation rate, N_w , has a value of zero except in the layer of sorbent particles which have accumulated at the droplet surface.

The boundary conditions of Eq. 21 are :

$$\begin{array}{ll} dc_L/dR = 0 & @ R = 0 \\ c_L = 0 & @ R = R_0 \end{array}$$

where R_0 is the radius of the reaction front. If the conditions within the droplet are such that the reaction front occurs at the droplet surface, the second boundary condition will be that the flux of dissolved hydroxide at the

surface equals the rate of external mass transfer with the concentration of SO_2 at the droplet surface equal to zero.

7.1.11 Solution of Concentration Profiles

The location of the reaction front within the droplet cannot be calculated a priori. The calculation of calcium and sulfur liquid phase concentration profiles within the droplet therefore involves a trial and error procedure. Three general cases must be considered:

1) If the rate of calcium dissolution is relatively slow, then sulfur species will penetrate to the center of the droplet and an HSO_3^- concentration will be guessed at the droplet center and the gas phase SO_2 concentration (which is known) calculated using Eq. 20 and its outer boundary condition. If the calculated gas phase SO_2 concentration is incorrect, then the sulfur species concentration at the droplet center is corrected by the secant method and the gas phase SO_2 concentration recalculated. This is continued until the calculated gas phase SO_2 concentration is correct.

2) If the rate of sorbent utilization is relatively fast, then the liquid phase sulfur species concentration will drop to zero at some point within the droplet. The solution approach for this case will be the same except that rather than guessing and adjusting the concentration at the droplet center, the radius where the liquid phase sulfur concentration falls to zero (the reaction front) is guessed. The dissolved calcium hydroxide profile must first be calculated in order to determine the boundary condition at the reaction front:

An iterative procedure is used where the dissolved calcium hydroxide at the droplet center is guessed, the concentration at the reaction front calculated using Eq. 21, and the guessed concentration at the droplet center corrected with the secant method. This is continued until the concentration of dissolved calcium hydroxide at the reaction front equals zero.

The gas phase SO_2 concentration is then calculated using Eq. 18 and its outer boundary condition. If the calculated gas phase SO_2 concentration is incorrect, then the radius of the reaction front is corrected by the secant method and the solution procedure (including solving for the calcium profile) repeated. This is continued until the calculated gas phase SO_2 concentration is correct.

3) If the rate of sorbent utilization is very fast, then the liquid phase sulfur species concentration may drop to zero at the droplet surface. The concentration profile of dissolved calcium hydroxide is then solved using the procedure described in case 2 but with the concentration of calcium at the droplet surface corrected so that the flux of dissolved calcium hydroxide equals the rate of external mass transfer with the concentration of SO_2 at the droplet surface set to zero.

At each new differential step down the duct begins by solving for the first case and, if it can't be solved, going on to the other two cases.

Once the liquid phase calcium and sulfur concentration profiles have been found, then utilization of sorbent particles at all radial locations is calculated from the difference in flux into and out of each radial shell. The extent of sorbent utilization is monitored as a function of radial location. This in turn affects the liquid phase concentration profiles as the physical properties of the sorbent particles change (the film thickness around the sorbent particles becomes thinner due to the decreasing particle size and the roughness factor, σ , becomes smaller as the particles become smaller). The concentration of SO_2 is based on a mass balance with the local concentration determined from the initial SO_2 concentration and the extent of sorbent utilization.

7.2 Dry Injection/Condensation Model

Condensation occurs on dry sorbent particles when they are injected into a duct with an initial temperature less than the dew point of the duct gases and continues until the sorbent particle heats up to the dew point. As condensation occurs some of this moisture will be absorbed into the pore structure of the sorbent particles. The sorbent particle will continue to heat up beyond the dew

point to the duct gases temperature. Some of the condensed water will evaporate while the moisture which was absorbed into the pore structure will remain.

The rate of condensation and particle heat up are calculated using Eqs. 1 through 4. When the sorbent particle heats up to the dew point the condensation calculations are stopped and the evaporation of any water not adsorbed in the sorbents pore structure is ignored. Although this is not realistic, the amount of water is negligible and ignoring its evaporation will not influence the model's predictions.

Once moisture is present on the sorbent particle the reaction between calcium hydroxide and SO_2 begins. (Capture is known to occur in the absence of water but only at an extremely slow rate.) As the reaction proceeds a layer calcium sulfite builds up on the surface of the sorbent particle. Subsequent adsorption of SO_2 requires the diffusion of sulfur through this product layer. The rate of SO_2 uptake is calculated by the grain model:

$$\frac{dN_{\text{Ca}}}{dt} = \frac{\pi d_p^2 c_{s,\infty}}{\left[\frac{1}{\sigma k_r (X_c/X_{\text{max}})} + \frac{1}{k_m} \left[\frac{d_c}{d_p} \right]^2 + \frac{d_c}{D_s} \left[1 - \frac{d_c}{d_p} \right] \right]} \quad (22)$$

The kinetic rate constant, k_r , and the product layer diffusivity, D_s , have the same value as those in Eq. 17 which govern the reaction in a wet agglomerate.

The model is written in Fortran 77 for use on IBM compatible computers. The model is made up of seventeen subroutines and requires one batch file and one or more data files to run it. Operation of the model on systems other than DOS may require modifications to the read/write statements in the code. A listing of the model's code is given in Appendix 1. Major model variables are given in Appendix 2.

A flow chart of the model is given in Figure 8-1. The primary function of the various subroutines are:

DEC is the main subroutine where the names of input data files are read, distance is stepped down the duct, and decisions are made where to print out results.

INITIAL reads the input data file, does preliminary calculations, and prints out the initial values.

HEADING prints out a heading.

CHK determines the step size. Called from both DEC.FOR and RUN.FOR.

RUNGKUT does the Runge-Kutta calculations. FNC provides the values of the differential equations for use by the Runge-Kutta method. If drop temperatures change too fast the step size will be reduced. PDIF is also called from here.

PDIF calculates the diffusion of sorbent particles between radial shells. The diffusion between two radial shells which have reached close packing is ignored.

FITE calculates the volume of calcium sulfite deposited in the radial shells.

FNC calculates the values of five of the six differential equations used in RUNGKUT. The sixth, governing the rate of sorbent utilization is calculated in SUL. The subroutines PHY and FLX are also called from here.

ETA calculates the scavenging efficiency for use in FNC.

Figure 8-1. Flow chart of model.

SUL calculates the rate of sorbent utilization in terms of the rate of sorbent diameter decrease.

PHY calculates a large number of physical constants for use in a number of other subroutines. Calls DELR.

DELR calculates the size of the differential radial shells based on the number of sorbent particles and volume of water in the shell.

FLX calculates the liquid phase sulfur profile in slurry drops. When the liquid phase sulfur profile cannot be solved CA is called and simultaneous liquid phase calcium and sulfur profiles are calculated. If calcium exists at the droplet surface a sulfur profile is not calculated. Liquid phase calcium profiles are calculated based on a different set of differential radial shells than those which keep track of the position of sorbent particles.

DIFF calculates the value of the differential equation which governs the diffusion of liquid phase sulfur.

DEL calculates film thickness around sorbent particles for DIFF.

CA calculates the liquid phase calcium profile in slurry drops.

CADIF calculates the value of the differential equation which governs the diffusion of liquid phase calcium.

PRINT prints out two types of results: general variables as a function of distance down the duct; and individual drop variables at distances in the duct specified by the operator.

Input parameters (duct dimensions, duct temperature, SO₂ concentrations, spray size distribution, etc.) are input through a data file using a DOS editor. The name of the data file is up to the operator.

9.1 Slurry Injection

9.1.1 Input

A copy of a sample input data file is given in Figure 9-1. Each input parameter in the data file is listed on a separate line. A space, or a tab, and an explanation follows each input parameter. The number in parentheses following the explanation was typed on Figure 9-1 to make this discussion easier. The majority of input parameters are self explanatory and need no discussion. The first two input parameters describe the sorbent properties. Inputting a surface area of 0 will give a default value of 15 m²/g. The third input parameter describes the injection strategy used: a slurry spray (s); humidification followed by dry injection of the sorbent (d); and dry injection of the sorbent followed by a spray (any letter other than "s" or "d"). A single letter, either upper or lower case, is used.

Input parameter 7 is the percent of sorbent recycled from the particulate collection device. Calculations utilizing the recycle value assume that the recycle contains the ash entered on line 6. Input parameter 8 is the percent utilization of sorbent in the recycle. This value must be initially guessed and then corrected in subsequent runs. An acceptable initial value for multi-sized sprays can be found by running the model several times with a single drop diameter equal to the mass mean diameter of the multi-sized spray and re-entering the output utilization from the previous run until the entered initial utilization approximately equals the calculated utilization at the end of duct.

Figure 9-1. Sample listing of input data file.

15	Sorbent surface area (m ² /g)	(1)
4.	Sorbent particle size (microns)	(2)
S	Slurry (s), Dry (d), or scavenging (any other letter)	(3)
1.0	Calcium to Sulfur ratio	(4)
10	Average diameter of ash in duct (micron)	(5)
700	Ash mass flow rate (g/sec)	(6)
25	% Sorbent recycled	(7)
40	% Utilization of sorbent in recycle	(8)
.091	Water mole fraction in duct gases	(9)
.1011	CO ₂ mole fraction in duct gases	(10)
144.65	Gas mass flow rate (Kg/sec)	(11)
30	Duct Length (m)	(12)
14.25	Duct cross-sectional area (m ²)	(13)
D	Direction of gas flow, (u)p, (d)own, or (h)orizontal	(14)
437.8	Gas temperature (K)	(15)
295	Drop temperature (K), initial	(16)
1	Pressure (atm)	(17)
1500	ppm SO ₂	(18)
5450	Water spray rate (g/sec)	(19)
60	Velocity of spray, initial (m/sec)	(20)
N	Allows droplets to have varying initial velocities (Y or N)	(21)
3	Number of drop sizes in distribution (15 maximum)	(22)
16.6,.277	Drop size (microns), weight fraction, initial velocity	(23)
33.6,.565		
63.1,.158		
2	Number of positions where drop variables will be printed	(24)
1.0	Distance to " " " " " " "	(25)
2.5		

Following the spray velocity (which gives all droplets the same initial velocity) is input parameter 21 which allows the droplets to have individual initial velocities. Input parameter 22 is the number of droplets of varying size which make up the spray. Although up to 15 different drop sizes may be used, using large numbers of drop sizes significantly increases the computer time it takes to run a case. A drop size distribution containing 3 or 4 drop sizes is suggested for most purposes. If, however, the purpose of running the model is to determine if any of the spray remains unevaporated at any position in the duct, than more drop sizes should be used. More drop sizes should be used especially in the larger size ranges where complete evaporation takes the longest. Following the number of drop sizes is the drop size distribution itself. Beginning with line 23, each drop size of the drop size distribution is input on a separate line as the drop size (microns) followed by a comma and the

weight fraction of each drop size. The sum of the weight fractions should equal one. The number of lines of the individual drop sizes must equal the number of drop sizes entered on line 22. A measured drop size distribution for a nozzle tested at EER is given as an example. If input parameter 21 was answered yes, then a comma and the individual drop velocities (m/sec) would be entered after the weight fraction of the drop size distribution. For example the first drop size of input parameter 23 would be entered as:

16.6,.277,35 Drop size (microns), weight fraction, initial velocity

The local properties of the drop size distribution may be printed out at any location in the duct. These include drop diameter, temperature, residence time, velocity, and the average utilization of sorbent in the droplet. The number of positions where this option is desired is entered in input parameter 24. The distances where this option is desired are entered on individual lines beginning at input parameter 25 and below. The number of lines below input parameter 24 must be greater than or equal to the value entered at input parameter 24.

9.1.2 Operation

The name of the data file to be run is entered in a file which must be named NAME.DAT. The model may be run in a batch mode by entering more than one data file in NAME.DAT. Two versions of the model were made available at the end of the contract: FDEC and DEC. FDEC is a faster version of DEC. This is accomplished by solving for the calcium and sulfur liquid phase concentration profiles less often. The slower version, DEC, was provided in case any stability problems were encountered with FDEC. The command to run the model is DEC>output. Model output will be stored in the file entered after the greater than sign. Any name can be selected for the output file. As the model runs a partial output will also be directed to the screen.

9.1.3 Output

The stored model output of the data file given in Figure 9-1 is given in Figure 9-2. The model calculation times for this case were 4 minutes for FDEC

and 6 minutes for DEC on a 386 based PC. The model lists the input data file followed by the input data. The model then lists distance down the duct in meters, gas residence time in seconds, fraction of the spray unevaporated, average percent sorbent utilization for the spray, percent SO₂ capture, temperature of the duct gases in degrees Kelvin, approach to saturation in degrees Kelvin, the number of drop sizes which have not yet evaporated, and the humidity in mole fraction. The average percent sorbent utilization includes the recycled sorbent and therefore has an initial value greater than zero. It should be noted that at .01 meters, at the beginning of the duct, that the fraction of spray unevaporated increases to 1.006. This results from the drop having an initial temperature below the dew point of the duct gases. Moisture condenses on the drop until the drop temperature rises above the dew point. Once a drop has evaporated SO₂ capture continues to occur in the agglomerate which has resulted from the evaporation of the slurry drop. This can be seen in Figure 9-2 when all of the spray has evaporated (#Wet = 0) and the SO₂ capture continues to increase.

At the end of the duct the final properties of the spray are printed. This gives the final size of the drop (now an agglomerate), weight fraction of the original spray still contained in the drop, drop temperature in degrees Kelvin, residence time of the drop when it evaporated, drop velocity, and average sorbent utilization in the drop.

Utilization of the sorbent at the end of the duct was calculated to be 50.3%. This is greater than that entered in the input file, 40%. This case should be rerun with a new initial utilization of the recycled sorbent. A new initial guess of 55% would be appropriate. Predicted SO₂ capture should not change substantially unless slurry concentrations are low.

9.2 Sorbent Injection Followed By Spray

To run the model for this injection strategy change input parameter 3 in Figure 9-1 to any letter but "S" or "D". An example of the output for this input data is given in Figure 9-3. The calculation time for this case was 6 minutes (FDEC) on a 386 based PC which is longer than for the slurry case. This longer calculation time results from the extra time it takes to solve both the internal

Input file=J12.DAT

Sorbent Diameter = 4.00 microns
 Sorbent Surf Area= 15.00 m2/g
 Ca/S = 1.00
 Effective Ca/S = 1.20 (Due to recycle, calculated)
 Initial Ave.Util.= 10.00 % (Due to recycle, calculated)
 Slurry Conc. = 10.10 % Wt. (sorbent only, calculated)
 SO2 Concentration= 1500.00 ppm
 Recycle = 25.00 % Wt. of Duct Output
 Util. of Recycle = 40.00 %
 Ash in Recycle = 49.80 % Wt. (calculated)
 Total Solids Conc= 15.67 % Wt. (calculated)
 Ave. Ash Diameter= 10.00 microns
 Ash Mass Rate = 700.00 g/sec
 Gas Mass Rate = 144.65 kg/sec
 Gas Temperature = 437.80 K
 Gas Humidity = 9.10 %
 Gas CO2 Conc. = 10.11 %
 Duct Area = 14.25 m2
 Duct Length = 30.00 m
 Water Mass Rate = 5450.00 g/sec
 Water Velocity = 60.00 m/sec
 Gas flow direction is down

Drop Size Distribution:

Drop Diameter (Microns)	Weight Fraction
16.6	0.277
33.6	0.565
63.1	0.158

Dist	Time	Frac Unevap	%Util	%SO2 Cap	Gas Temp	App/Sat	#Wet	Humidity
0.01	0.001	1.006	10.02	0.039	435.2	117.8	3	.0906
0.02	0.002	1.002	10.06	0.089	433.9	116.5	3	.0909
0.03	0.002	0.993	10.09	0.149	432.7	115.2	3	.0914
0.04	0.003	0.982	10.14	0.222	431.5	113.8	3	.0920
0.05	0.004	0.968	10.19	0.309	430.1	112.3	3	.0928
0.06	0.005	0.954	10.25	0.406	428.8	110.8	3	.0936
0.07	0.006	0.940	10.32	0.512	427.4	109.3	3	.0944
0.08	0.007	0.926	10.39	0.624	426.1	107.8	3	.0952
0.09	0.007	0.912	10.45	0.727	424.8	106.3	3	.0959
0.10	0.008	0.897	10.52	0.835	423.5	104.9	3	.0967
0.20	0.017	0.762	11.7	2.66	411.2	91.1	3	.1042
0.30	0.025	0.648	15.1	8.19	401.1	79.9	3	.1103
0.40	0.034	0.569	17.7	12.33	394.2	72.2	3	.1146
0.50	0.043	0.529	18.6	13.80	390.7	68.4	3	.1167
0.60	0.051	0.491	19.9	15.80	387.4	64.8	3	.1187
0.70	0.060	0.456	21.7	18.77	384.4	61.4	3	.1206
0.80	0.069	0.423	23.7	21.90	381.6	58.4	3	.1223
0.90	0.078	0.393	25.6	24.97	379.0	55.5	3	.1239
1.00	0.087	0.364	27.5	27.96	376.6	52.8	3	.1254

At 1.001 meters the individual drop parameters are:

Drop Diam	Frac Water	%Water	Drop Temp	Drop Time	Drop Vel	% Util	%Ash
57.96	0.131	78.83	326.8	0.058	11.32	15.89	7.0
25.89	0.224	63.52	326.8	0.078	11.11	33.32	9.8
8.15	0.009	12.67	376.7	0.030	11.14	34.77	21.0

Dist	Time	Frac Unevap	%Util	%SO2 Cap	Gas Temp	App/Sat	#Wet	Humidity
2.00	0.179	0.164	41.1	49.71	359.8	34.5	2	.1357
2.52	0.226	0.131	42.5	51.94	357.1	31.5	1	.1373

At 2.516 meters the individual drop parameters are:

Drop Diam	Frac Water	%Water	Drop Temp	Drop Time	Drop Vel	% Util	%Ash
32.79	0.102	72.62	357.6	0.197	10.75	35.51	8.3
17.15	0.020	12.42	357.2	0.191	10.69	59.57	21.1
8.15	0.009	12.66	357.2	0.030	10.67	34.99	21.0

Dist	Time	Frac Unevap	%Util	%SO2 Cap	Gas Temp	App/Sat	#Wet	Humidity
3.02	0.274	0.123	43.3	53.21	356.5	30.9	1	.1377
4.02	0.368	0.109	44.4	55.03	355.3	29.6	1	.1384
5.02	0.463	0.096	46.0	57.55	354.3	28.4	1	.1391
6.02	0.557	0.084	46.6	58.54	353.3	27.3	1	.1397
7.02	0.652	0.073	47.4	59.84	352.4	26.3	1	.1403
8.02	0.748	0.063	48.1	60.92	351.6	25.5	1	.1408
9.02	0.843	0.053	48.5	61.58	350.8	24.6	1	.1412
10.00	0.937	0.045	48.8	62.05	350.2	23.9	1	.1416
10.02	0.938	0.045	48.8	62.06	350.2	23.9	1	.1416
12.52	1.178	0.036	49.1	62.63	349.4	23.1	0	.1421
15.02	1.417	0.036	49.3	62.94	349.4	23.1	0	.1421
17.52	1.656	0.036	49.3	63.23	349.4	23.1	0	.1421
20.02	1.896	0.036	49.7	63.51	349.4	23.1	0	.1421
22.52	2.135	0.036	49.9	63.78	349.4	23.1	0	.1421
25.02	2.374	0.036	50.0	64.05	349.4	23.1	0	.1421
27.52	2.613	0.036	50.2	64.30	349.4	23.1	0	.1421
30.02	2.853	0.036	50.3	64.55	349.4	23.1	0	.1421

At 30.016 meters the individual drop parameters are:

Drop Diam	Frac Water	%Water	Drop Temp	Drop Time	Drop Vel	% Util	%Ash
33.42	0.006	12.35	349.4	1.027	10.54	81.15	22.5
17.15	0.020	12.32	349.4	0.191	10.51	61.92	21.0
8.15	0.009	12.50	349.4	0.030	10.49	38.28	20.7

Figure 9-2. Model output for the input data file given in Figure 9-1.

Input file=J12B.DAT

Sorbent Diameter = 4.00 microns
 Sorbent Surf Area = 15.00 m2/g
 Ca/S = 1.00
 Effective Ca/S = 1.20 (Due to recycle, calculated)
 Initial Ave.Util. = 10.00 % (Due to recycle, calculated)
 Sorbent Mass Rate = 652.79 g/sec (calculated)
 SO2 Concentration = 1500.00 ppm
 Recycle = 25.00 % Wt. of Duct Output
 Util. of Recycle = 40.00 %
 Ash in Recycle = 49.80 % Wt. (calculated)
 Ave. Ash Diameter = 10.00 microns
 Ash Mass Rate = 700.00 g/sec
 Gas Mass Rate = 144.65 kg/sec
 Gas Temperature = 437.80 K
 Gas Humidity = 9.10 %
 Gas CO2 Conc. = 10.11 %
 Duct Area = 14.25 m2
 Duct Length = 30.00 m
 Water Mass Rate = 5450.00 g/sec
 Water Velocity = 60.00 m/sec
 Gas flow direction is down

Drop Size Distribution:

Drop Diameter (Microns)	Weight Fraction
16.6	0.277
33.6	0.565
63.1	0.158

Dist	Time	Frac Unevap	XScav	XSO2 Cap	Gas Temp	App/Sat	#Wet	Humidity
0.01	0.001	1.005	1.28	0.000	435.5	118.1	3	.0907
0.02	0.002	1.000	2.45	0.001	434.3	116.9	3	.0910
0.03	0.002	0.992	3.48	0.003	433.2	115.7	3	.0915
0.04	0.003	0.980	4.34	0.007	432.0	114.4	3	.0921
0.05	0.004	0.967	5.04	0.011	430.8	113.0	3	.0928
0.06	0.005	0.954	5.65	0.017	429.5	111.5	3	.0936
0.07	0.006	0.941	6.20	0.023	428.2	110.1	3	.0943
0.08	0.007	0.927	6.71	0.030	427.0	108.7	3	.0951
0.09	0.007	0.914	7.18	0.038	425.8	107.4	3	.0958
0.10	0.008	0.901	7.61	0.047	424.6	106.0	3	.0965
0.20	0.017	0.773	9.86	0.183	413.0	93.0	3	.1034
0.30	0.025	0.667	10.56	1.504	403.6	82.6	3	.1093
0.40	0.034	0.584	11.00	1.992	396.3	76.5	3	.1138
0.50	0.042	0.531	11.24	2.284	391.7	69.4	3	.1166
0.60	0.051	0.496	11.35	2.453	388.6	66.0	3	.1185
0.66	0.056	0.476	11.38	2.557	386.9	64.1	3	.1195
0.70	0.060	0.463	11.6	2.63	385.8	62.9	3	.1202
0.80	0.069	0.432	11.8	2.88	383.2	60.0	3	.1218
0.90	0.078	0.404	13.0	4.77	380.8	57.3	3	.1233
1.00	0.087	0.377	13.8	6.08	378.5	54.8	3	.1247

At 1.001 meters the individual drop parameters are:

Drop Diam	Frac Water	%Water	Drop Temp	Drop Time	Drop Vel	% Util	%Ash
60.15	0.132	92.79	326.8	0.060	11.33	18.33	4.0
35.74	0.243	90.96	326.8	0.079	11.14	56.35	4.4
4.09	0.001	12.92	378.6	0.038	11.10	79.49	39.7

Dist	Time	Frac Unevap	XUtil	XSO2 Cap	Gas Temp	App/Sat	#Wet	Humidit
2.00	0.178	0.187	15.8	9.29	362.6	37.4	2	.1345
2.50	0.225	0.131	16.6	10.62	358.0	32.4	2	.1373

At 2.501 meters the individual drop parameters are:

Drop Diam	Frac Water	%Water	Drop Temp	Drop Time	Drop Vel	% Util	%Ash
55.68	0.104	90.24	327.6	0.197	10.78	49.24	5.0
13.66	0.027	49.91	327.6	0.217	10.66	94.15	22.4
4.09	0.001	12.92	358.0	0.038	10.65	79.54	39.7

Dist	Time	Frac Unevap	XUtil	XSO2 Cap	Gas Temp	App/Sat	#Wet	Humidit
3.01	0.271	0.102	16.9	11.11	355.6	29.8	1	.1388
4.01	0.366	0.089	17.1	11.43	354.5	28.6	1	.1394
5.01	0.461	0.077	17.4	11.87	353.6	27.6	1	.1400
6.01	0.555	0.067	17.6	12.19	352.7	26.6	1	.1406
7.01	0.651	0.057	17.7	12.37	351.9	25.8	1	.1411
8.01	0.746	0.048	17.9	12.60	351.2	25.0	1	.1415
9.01	0.841	0.039	17.9	12.71	350.5	24.2	1	.1419
10.01	0.937	0.032	18.0	12.82	349.9	23.6	1	.1423
12.51	1.176	0.019	18.1	13.96	348.7	22.2	1	.1431
15.01	1.416	0.007	18.1	15.00	347.9	21.3	0	.1436
17.51	1.655	0.007	18.1	13.02	347.9	21.3	0	.1436
20.01	1.895	0.007	18.1	13.04	347.9	21.3	0	.1436
22.51	2.135	0.007	18.2	13.05	347.9	21.3	0	.1436
25.01	2.375	0.007	18.2	13.07	347.9	21.3	0	.1436
27.51	2.615	0.007	18.2	13.09	347.9	21.3	0	.1436
30.01	2.855	0.007	18.2	13.10	347.9	21.3	0	.1436

At 30.008 meters the individual drop parameters are:

Drop Diam	Frac Water	%Water	Drop Temp	Drop Time	Drop Vel	% Util	%Ash
22.60	0.002	12.37	347.9	1.348	10.47	99.99	39.1
10.09	0.004	12.32	347.9	0.250	10.45	96.96	38.4
4.09	0.001	12.90	347.9	0.038	10.42	80.36	39.7

Figure 9-3. Model output for the input data file given in Figure 9-1 with input parameter 3 changed to the letter "a".

calcium and sulfur concentration profiles which occur when the slurry concentration in the droplet is low (as compared to solving only the calcium profile when slurry concentrations are high). The predicted capture in Figure 9-3 is also much less than that predicted for the slurry injection in Figure 9-2. This is a result of the low amount of sorbent scavenged by the spray. Increasing the velocity of the spray, the calcium to sulfur ratio, or the amount of recycle would increase scavenging and therefore the extent of sorbent utilization.

9.3 Humidification

The SO₂ capture subroutines in the slurry model consume most of the computer's operating time. When the operator is interested in only running humidification calculations the SO₂ capture subroutines can be turned off by entering either an SO₂ concentration or a calcium to sulfur ratio of zero.

9.4 Sorbent Injection After Humidification

The dry injection/condensation model considers only the condensation of water on a sorbent particle and the subsequent reaction with SO₂. Humidification calculations must be done in separate runs.

A copy of a sample input data file is given in Figure 9-4. This input file differs from that for the slurry injection case in Figure 9-1 in that input parameter 3 has been changed to "D", the gas temperature has been changed, and input parameters 19 through 25 are absent. A copy of the model output for the data file in Figure 9-4 is given in Figure 9-5. The model calculation time for this case was 20 seconds on a 386 based PC.

In Figure 9-5 the model lists the input data file followed by the input for the data file. The model then lists distance down the duct in meters, gas residence time in seconds, the ratio of moles condensed on the particle divided by the moles calcium hydroxide, percent sorbent utilization for the spray, and percent SO₂ capture. It should be noted that the model parameters used in making the predictions in Figure 9-5 have not been accurately calibrated against fundamental or pilot scale data. When an ESP follows the duct, SO₂ capture may also be greater than predicted since the gas residence time in an ESP is on the

order of 10 seconds, roughly three times that available in this hypothetical duct. This may be allowed for by increasing the length of the duct by so that the total calculated residence time equals the sum of the residence time in the duct and the ESP.

Figure 9-4. Sample listing of input data file.

15	Sorbent surface area (m ² /g)	(1)
4.	Sorbent particle size (microns)	(2)
D	Slurry (s), Dry (d), or scavenging (any other letter)	(3)
1.0	Calcium to Sulfur ratio	(4)
10	Average diameter of ash in duct (micron)	(5)
700	Ash mass flow rate (g/sec)	(6)
25	% Sorbent recycled	(7)
40	% Utilization of sorbent in recycle	(8)
.091	Water mole fraction in duct gases	(9)
.1011	CO ₂ mole fraction in duct gases	(10)
144.65	Gas mass flow rate (Kg/sec)	(11)
30	Duct Length (m)	(12)
14.25	Duct cross-sectional area (m ²)	(13)
D	Direction of gas flow, (u)p, (d)own, or (h)orizontal	(14)
337.8	Gas temperature (K)	(15)
295	Particle temperature (K), initial	(16)
1	Pressure (atm)	(17)
1500	ppm SO ₂	(18)

Input file=T1.DAT

Sorbent Diameter = 4.00 microns
 Sorbent Surf Area= 15.00 m2/g
 Ca/S = 1.00
 Effective Ca/S = 1.20 (Due to recycle, calculated)
 Initial Ave.Util.= 10.00 % (Due to recycle, calculated)
 Sorbent Mass Rate= 667.72 g/sec (calculated)
 SO2 Concentration= 1500.00 ppm
 Recycle = 25.00 % Wt. of Duct Output
 Util. of Recycle = 40.00 %
 Gas Mass Rate = 144.65 Kg/sec
 Gas Temperature = 337.80 K
 Gas Humidity = 15.10 %
 Gas CO2 Conc. = 10.11 %
 Duct Area = 14.25 m2
 Duct Length = 30.00 m
 App. To Sat. = 10.24 K (calc.)
 Gas flow direction is horizontal

Dist	Time	Mole Conden	%Util	%SO2 Cap
0.01	0.001	0.178	10.02	0.027
0.02	0.002	"	10.04	0.057
0.03	0.003	"	10.05	0.087
0.04	0.004	"	10.07	0.117
0.05	0.005	"	10.09	0.146
0.06	0.006	"	10.11	0.176
0.07	0.007	"	10.13	0.205
0.08	0.008	"	10.15	0.234
0.09	0.009	"	10.16	0.263
0.10	0.010	"	10.18	0.292
0.20	0.021	"	10.36	0.578
0.30	0.031	"	10.53	0.855
0.40	0.041	"	10.70	1.123
0.50	0.051	"	10.86	1.383
0.60	0.062	"	11.02	1.636
0.70	0.072	"	11.18	1.881
0.80	0.082	"	11.3	2.12
0.90	0.092	"	11.5	2.35
1.00	0.103	"	11.6	2.58
2.00	0.205	"	12.8	4.55
3.00	0.308	"	13.8	6.14
4.00	0.411	"	14.7	7.46
5.00	0.513	"	15.4	8.60
6.00	0.616	"	16.0	9.60
7.00	0.718	"	16.6	10.50
8.00	0.821	"	17.1	11.30
9.00	0.924	"	17.5	12.04
9.99	1.025	"	17.9	12.72
10.00	1.026	"	18.0	12.72
12.50	1.283	"	18.9	14.23
15.00	1.540	"	19.7	15.52
17.50	1.796	"	20.4	16.67
20.00	2.053	"	21.1	17.70
22.50	2.309	"	21.7	18.64
25.00	2.566	"	22.2	19.51
27.50	2.822	"	22.7	20.33
30.00	3.079	"	23.2	21.09

At 30.000 meters the individual drop parameters are:

Drop Diam	Frac Water	%Water	Drop Temp	Drop Time	Drop Vel	% Util	%As
1.99	0.009	4.03	337.4	3.079	9.74	44.46	0.
1.83	0.036	3.65	337.6	3.079	9.74	19.60	0.

Figure 9-5. Model output for the input data file given in Figure 9-4.

The rate controlling subprocesses are summarized for a range of drop sizes in Figure 10-1 by plotting the calculated rate of sulfur absorption divided by the maximum rate of external mass transfer possible. Liquid phase mass transfer of the sulfur species controls the overall rate at the beginning (before sorbent particles have accumulated at the droplet surface) and at the end (when sorbent at the surface has been consumed) of the lifetime of droplets larger than $\sim 20 \mu\text{m}$. External mass transfer is rate controlling over the intervening portion of their lifetime. Liquid phase mass transfer of sulfur species also initially controls the overall rate of droplets under $20 \mu\text{m}$. Throughout the remainder of their life the rate of liquid phase mass transfer (both calcium and sulfur) in the film surrounding the sorbent particles is rate limiting. (It should be noted that the rate controlling subprocesses will also vary as other parameters such as slurry concentration or SO_2 concentration change.)

Data is available as a function of two process parameters. Predicted SO_2 capture as a function of stoichiometric ratio is compared against data obtained from duct dry scrubbing pilot scales studies in Figure 10-2. Agreement between the data and model is excellent. The size distribution used in these calculations is given in Table 10-1, was measured for a two-fluid nozzle typical of those used in a stoichiometric ratio of one and levels off at higher ratios. Two factors contribute to this trend. Increasing the stoichiometric ratio is equivalent to increasing the slurry concentration. At stoichiometric ratios above 1.0 increasing the slurry concentration will improve SO_2 capture only during the initial portions of the droplet's life (Figure 10-1) by increasing the concentration of sorbent particles near the droplet surface and thus reducing the resistance to liquid phase mass transfer. Throughout the remainder of the droplet's life the rate of SO_2 capture is limited by either external mass transfer or by liquid phase mass transfer of sulfur species through a layer of calcium sulfite particles. Increasing the slurry concentration has no effect on these processes.

Figure 10-1. Relative rate of SO_2 sorption as a function of droplet initial diameter and relative lifetime.

Figure 10-2. Prediction and measured pilot-scale SO₂ capture as a function of the normalized stoichiometric ratio of sorbent slurry to SO₂.

TABLE 10-1. TYPICAL SPRAY SIZE DISTRIBUTION

Drop Size (μm)	Weight Fraction
16.6	.277
33.6	.565
63.1	.158

The second factor which influences the rate of SO_2 capture is the increase in the solids content of the slurry droplets. Increasing the solids content increases the number of droplets which in turn increases the surface area available for both external mass transfer of SO_2 and evaporation. The increased evaporation rate results in a reduced droplet lifetime which tends to negate the increased rate of external mass transfer.

The agreement between literature data taken as a function of approach to saturation and model predictions, illustrated in Figure 10-3, is excellent. The primary cause of the trends observed in Figure 10-3 is the increase in droplet lifetime as the approach to saturation is decreased. A secondary factor which contributes to these trends is the increase in the quantity of spray increases the surface area available for external mass transfer and decreases the slurry concentration, both of which tend to increase utilization.

Figure 10-3. Model predictions compared with pilot-scale data showing the impact of approach to saturation of in-duct injection slurry utilization.

a	=	Activity of water
A	=	Surface area of sorbent
A_s	=	Surface area of a sorbent particle if it were a sphere with no porosity
c	=	Concentration
c_1	=	Concentration of HSO ₃ ⁻
c_{2*}	=	Concentration of H ₂ SO ₃
c_L	=	Lime concentration at sorbent surface
c_n	=	Particle number concentration
C_p	=	Heat capacity
$c_{s,\infty}$	=	Concentration of SO ₂ in the bulk gas phase
d_c	=	Diameter of shrinking core of sorbent particles, used in Eq. 20
d_p	=	Sorbent particle diameter
D	=	Drop diameter
D_1	=	Liquid phase diffusivity of HSO ₃ ⁻
D_2	=	Liquid phase diffusivity of H ₂ SO ₃
D_p	=	Diffusivity of sorbent particles
D_w	=	Bulk diffusivity of water vapor
D_L	=	Liquid phase diffusivity of calcium hydroxide
e_p	=	Sorbent number concentration (#/m ³)
f	=	Drop number flux
F	=	Mass flux
h	=	Heat transfer coefficient
ΔH_R	=	Heat of reaction
H_e	=	Henry's constant
k	=	Thermal conductivity
k_b	=	Boltzmann's constant
k_d	=	Dissolution rate constant at sorbent surface
k_m	=	Mass transfer coefficient (SO ₂)
k_r	=	Chemical reaction rate constant for the lime-SO ₂ reaction in the wet agglomerate and condensation reactions
k_w	=	Mass transfer coefficient (water)
K_d	=	Dissociation constant of H ₂ SO ₃
m	=	Mass

M	=	Molecular weight
n	=	Number of sorbent particles in a drop
N	=	Scavenging efficiency
N_w	=	Evaporation rate
N_{Ca}	=	Moles calcium
r_c	=	Radius of water core in a drying agglomerate
r_s	=	Radius of agglomerate
R	=	Radial position within droplet
t	=	Time
T	=	Temperature
V'	=	Molar volume of $Ca(OH)_2$
V	=	Velocity
V_s	=	Fraction volume of solids in a radial shell
w	=	Volume fraction water in a drop
x	=	Mole fraction of water vapor
X_c	=	Mole fraction water condensed on a sorbent particle with a maximum allowable value of X_{max} , used in Eq. 20
X_m	=	Mole fraction dissolved solids
X_{max}	=	Empirically set amount of water absorbed by pore structure which cannot evaporate, used in Eq. 20
y	=	Axial distance
Y	=	Sulfur dioxide mole fraction in the gas phase

Greek Letters

δ	=	Film thickness which calcium must diffuse outward from sorbent particle when diffusion of SO_2 to particle is considered
δ'	=	Film thickness around a sorbent particle
ϵ	=	Sorbent porosity
ρ	=	Density
μ	=	Viscosity
σ	=	Roughness factor

Subscripts

a	-	Agglomerate
-----	---	-------------

c	-	Critical
d	-	Drop
ds	-	Drop surface
e	-	Equilibrium
f	-	Film
g	-	Gas
i	-	Drop i
L	-	Lime
o	-	Initial
p	-	Particle
s	-	Sorbent
w	-	Water
•	-	Bulk gas

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APPENDIX 1

LISTING OF COMPUTER CODE

C Initialize variables and print output headings.

```
IJJ=0  
CALL INITIAL(III,PSDPt,DuctLength,VAR,PD,IJJ)  
IF(IJJ.EQ.1) GO TO 866
```

```
CLOSE(UNIT=24)
```

C Initialize operational variables.

```
J=1  
ID=0  
Dist=0  
IPSD=0  
ICLK=0  
IHED=0  
IF(Slu.NE.'D') ICLK=1  
IPRNT=0  
IWARN=0  
ICEASE=0  
PRNTSTP=.01
```

C Determine the initial step size.

```
CALL CHK(H,Dist,VAR)
```

C Perform numerical calculations.

```
50  CONTINUE  
    IF(Slu.EQ.'A'.AND.IHED.EQ.0.AND.ABS(VAR(4,NW)-GV).LT.1) THEN  
        PRINT *  
        CALL PRINT(Dist,VAR,PD,ID,1)  
        IHED=1  
        CALL HEADING  
    ENDIF  
  
    CALL RUNGKUTT(VAR,PD,Dist,H,IWARN)  
    IF(ICEASE.EQ.1) GO TO 867  
    Dist=Dist+H  
    dis=dist
```

C For dry sorbent/condensation case change step size when condensation
C has ceased.

C Change frequency of printout with distance and adjust step size.

```
IF(Slu.EQ.'D'.AND.IDRY.EQ.1.AND.ICLK.EQ.0) THEN  
    H=1D-2  
    ICLK=1  
    IF(GV.LT.12) H=H/INT(16/GV)  
ENDIF
```

```
IF(Dist.GT..1-1D-5.AND.ICLK.EQ.1) THEN
```

```

    PRNTSTP=.1
    IF(Slu.EQ.'D'.AND.IDRY.EQ.1) THEN
        H=5D-3
    IF(GV.LT.12) H=H/INT(16/GV)
    ELSEIF(Slu.NE.'D') THEN
        CALL CHK(H,Dist,VAR)
    ENDIF
    ICHK=2
ELSEIF(Dist.GT.1-1D-4.AND.ICHK.EQ.2) THEN
    IF(Slu.EQ.'D'.AND.IDRY.EQ.1) THEN
        H=1D-1
        IF(GV.LT.12) H=H/INT(16/GV)
    ENDIF
    PRNTSTP=1
    ICHK=3
ELSEIF(Dist.GE.9.99.AND.ICHK.EQ.3) THEN
    ICHK=4
    PRNTSTP=2.5
ELSEIF(Dist.GE.39.99.AND.ICHK.EQ.4) THEN
    ICHK=5
    PRNTSTP=5
ELSEIF(Dist.GE.59.99.AND.ICHK.EQ.5) THEN
    PRNTSTP=10
ENDIF

```

C Print results if spray has evaporated.

```

    IF(IWARN.NE.0) THEN
    IF(IWARN.EQ.4) THEN
    PRINT *
    PRINT *, 'Spray has evaporated, final results:'
    PRINT 77, 'At distance=', Dist, ':'
    PRINT *
        CALL HEADING
77  FORMAT(A13,F7.3,A1)
    GO TO 867

```

C If program is diverging cease program execution.

```

    ELSEIF(IWARN.EQ.5) THEN
        PRINT *, 'IWARN=', IWARN
        GO TO 867
    ELSE

    PRINT 1
    PRINT *, 'PROGRAM HAS DIVERGED, FINAL OUTPUT:'
        PRINT *, 'Step Size=', H, ' meters'
        print *, 'iwarn= ', iwarn
    PRINT *
        CALL HEADING
        CALL PRINT (Dist,VAR,PD,ID,0)
    PRINT 1
    GO TO 867

```



```

      ENDIF
      ENDIF
1      FORMAT(1X,80('*'))

```

C Print drop variables at specifed distances.

```

      ipz=0
      IF(Dist.GT.DuctLength) GO TO 867
      IF(INT(Dist/PSDPt(J)).NE.IPSD) THEN
        CALL PRINT (Dist,VAR,PD,ID,0)
        J=J+1
        IPSD=Dist/PSDPt(J)
        IPRNT=Dist/PRNTSTP+1D-5
        CALL HEADING
      ipz=2
      GO TO 50
      ENDIF
      IPSD=Dist/PSDPt(J)

```

C Print results at varing distances.

```

      IF(INT(Dist/PRNTSTP+1D-5).NE.IPRNT) THEN
        CALL PRINT(Dist,VAR,PD,ID,1)
      ENDIF
      IPRNT=Dist/PRNTSTP+1D-5

```

```

      GO TO 50

```

```

867    CALL PRINT (Dist,VAR,PD,ID,0)
866    CONTINUE

```

```

      CLOSE(UNIT=2)
400    STOP
      END

```

SUBROUTINE INITIAL(III,PSDPt,DuctLength,VAR,PD,IJJ)

C Read input data and initialize variables.

REAL DropDiam(15),WF(15),CD0(15),DropNFlux(15),MolWt,NASH(15,50)
REAL VAR(7,15),NPartOld(15),dR(15,50),NPart(15,50),Rdry0(15,50)
REAL PSDPt(100),MWGO,DTime(15),DsSolids(15),PD(15,50),Tave(15)
REAL CO(15),dRSO2(15),ShellFlux(15,50),NPold(15)
REAL NASHOLD(15),PDOLD(15,50)
REAL *8 CCaO(15),RoId1(15)
INTEGER ISTOP(15),IVSTOP(15),IoId(15),NSHELL(15)
INTEGER Mevap(15),NStart(15)
CHARACTER*1 DIR,Slu,DAVE
CHARACTER*4 SorbType
CHARACTER*80 FILEIN

COMMON/FILE/FILEIN
COMMON/RKPR/NW,NE
COMMON/FN/DropNFlux,DuctArea,AirMassFlux,WVMFlux0
COMMON/DROP/DropDiam
COMMON/PP/P
COMMON/E/SD,PD0,SP,PDD
COMMON/P/CD0,SMFO
COMMON/I/ISTOP
COMMON/C/IVSTOP
COMMON/WF/WF
COMMON/PRNT/GV
COMMON/IoId/IoId
COMMON/VOL/Volmol,CaUt
COMMON/MOL/MolWt
COMMON/IMIN/IMIN
COMMON/DIR/IDir
COMMON/Y/SO2MFO
COMMON/T/Time
COMMON/CO2/CO2,MWGO
COMMON/SLU/Slu
COMMON/J/CAS/CaS
COMMON/DTIME/DTime
COMMON/DAVE/DAVE
COMMON/SA/RoughK
COMMON/TO/TO
COMMON/IDRY/IDRY
COMMON/IC/ICOUNT
COMMON/NP/NPartOld
COMMON/NPOLD/NPold
COMMON/DS/DsSolids
COMMON/NS/NSHELL
COMMON/DR/dR
COMMON/NPDR/NPart
COMMON/MEVAP/Mevap
COMMON/RD/Rdry0
COMMON/A/ALPHA
COMMON/NT/NStart

```

COMMON/AG/DissRate,RateK,Dprod
COMMON/CO/CO
COMMON/ROLD/Rold1
COMMON/SS/dRSO2
COMMON/SHEL/ShellFlux
COMMON/TAVE/Tave,NSTEPS
COMMON/DV/DelVO
COMMON/CCAO/CCaO
COMMON/NASH/NASH
COMMON/ASH/ASHFLUXO,DASH,ASHFLUX
COMMON/NAOLD/NASHOLD
COMMON/UTO/UTO,EFFCAS,PDRO
COMMON/PRE/PRECYCLE
COMMON/PDOLD/PDOLD
COMMON/IAT/IAT

```

C Input case data. Variables are:

```

C SorbType = Has no real use now. Enter as CHYD
C SurfArea = Surface area of sorbent in m2/g. Default value of 15 used
C   if 0 entered.
C CaUt = Fraction of calcium initially utilized by sulfur. For use when
C   boiler injection is followed by a scavenging spray.
C PD(I,M) = Sorbent Particle Diameter in microns.
C Slu = Indicates whether sorbent is present in the spray as a slurry(S)
C   as a Dry particle injected into a prehumidified duct (D), or as
C   a particle which will be scavenged by a spray (any letter but D
C   or S).
C CaS = Calcium to sulfur molar ratio.
C SP = Sorbent porosity. Usually entered as 0 for hydrated lime.
C DHum = Molar fraction of water in initially in the duct gases.
C CO20 = Molar fraction of CO2 initially in the duct gases (wet basis).
C GasMassRate = Mass flowrate of gases initially in the duct. In Kg/sec.
C Duct Length = Length of duct in meters.
C DuctArea = Cross sectional area of duct in sq. meters.
C DIR = Direction of flow in duct. Entered as Up, Down, or Horizontal.
C T0 = Intial temperature of duct gases in degrees Kelvin.
C DropTemp = Initial temperature of drops in degrees Kelvin.
C P = Pressure of duct in atmospheres.
C PPM = ppm SO2 in duct gases.
C WMRO = Rate of spray into duct in grams/sec.
C WaterVel = Velocity of spray in meters/sec.
C DAVE = Allows the velocity of different sized drops to be entered
C   independently. Entered either as Yes or No.
C NW = The number of drop sizes contained in the spray size distribution.
C DropDiam(I) = Diameter of drop in microns.
C WF(I) = Weight Fraction of each size of drops in the total spray. Sum
C   of WF(I) should equal 1.

```

```

SorbType='CHYD'
READ(24,*) SurfArea
CaUt=0
READ(24,*) PDO
READ(24,1) Slu

```

```

READ(24,*) CaS
SP=0
READ(24,*) DASH
IF(DASH.LE.0) DASH=10
READ(24,*) AshLoad
READ(24,*) PRECYCLE
READ(24,*) ReUt
READ(24,*) DHum
READ(24,*) CO2O
READ(24,*) GasMassRate
READ(24,*) DuctLength
READ(24,*) DuctArea
READ(24,1) DIR
READ(24,*) TO
READ(24,*) DropTemp
READ(24,*) P
READ(24,*) PPM
IF(Slu.EQ.'d') Slu='D'
READ(24,*) WMRO
READ(24,*) WaterVel
READ(24,1) DAVE
READ(24,*) NW
IF(Slu.EQ.'D') THEN
  WMRO=1
  WaterVel=1
  DAVE='N'
  NNW=NW
  NW=1
ENDIF
1  FORMAT(A1)
2  FORMAT(A4)
IF(CAS.EQ.0) PPM=0
IF(Slu.NE.'D'.AND.WMRO.EQ.0) THEN
  PRINT *, 'Spray Rate = 0. Program Terminated.'
  IJJ=1
  RETURN
ELSEIF(Slu.EQ.'D'.AND.DHum.EQ.0) THEN
  PRINT *, 'Humidity = 0. No condensation will occur. Program'
  &      ', Terminated.'
  IJJ=1
  RETURN
ENDIF

```

C Change letter variables to capitals.

```

IF(Slu.EQ.'s') Slu='S'
IF(Slu.NE.'S'.AND.Slu.NE.'D') Slu='A'
IF(DIR.EQ.'u') DIR='U'
IF(DIR.EQ.'d') DIR='D'
IF(DAVE.EQ.'n') DAVE='N'
IF(DAVE.EQ.'y') DAVE='Y'

```

C Read drop size distribution.

```

IF(Slu.EQ.'D') THEN
  NN=NNW
ELSE
  NN=NW
ENDIF
DO 10,I=1,NN
  IF(DAVE.EQ.'N') THEN
    READ(24,*) DropDiam(I),WF(I)
  ELSEIF(DAVE.EQ.'Y') THEN
    READ(24,*) DropDiam(I),WF(I),VAR(4,I)
  ELSE
    PRINT *,'*DAVE(Y,N) OR Slu(S,A,D) VARIABLES INPUT IMPROPERLY*'
    RETURN
  ENDIF
ENDIF

```

```

IF(Slu.EQ.'D') THEN
  NW=1
  WF(1)=1
  DropDiam(1)=PDO
  IF(PRECYCLE.NE.0) THEN
    ALPHA=1.5519
    DropDiam(2)=(ALPHA*PDO**3*ReUt/100+PDO**3*(1-ReUt/100))
    &      ** .3333333333*1E-6
    NW=2
  ENDIF
ENDIF

```

C Initialize drop variables and convert sizes from microns to meters.

```

  ISTOP(I)=0
  Iold(I)=0
  DTime(I)=0
10  DropDiam(I)=DropDiam(I)*1E-6
    PDO=PDO*1E-6
    DASH=DASH*1E-6
    PRECYCLE=PRECYCLE/100
    ReUt=ReUt/100

```

C Read distances where drop variables are to be printed out.

```

  READ(24,*) NPSD
  DO 20,I=1,NPSD
20  READ(24,*) PSDPt(I)
    PSDPt(NPSD+1)=DuctLength+1

```

C Order drop size distribution from small to large drops.

```

IF(Slu.NE.'D') THEN
  DO 15,I=1,NW
  DO 16,J=I+1,NW
  IF(DropDiam(I).GT.DropDiam(J)) THEN
    DUM=WF(I)
    WF(I)=WF(J)
    WF(J)=DUM
  
```

```

      DUM=DropDiam(I)
      DropDiam(I)=DropDiam(J)
      DropDiam(J)=DUM
      IF(DAVE.EQ.'Y') THEN
      DUM=VAR(4,I)
      VAR(4,I)=VAR(4,J)
      VAR(4,J)=DUM
      ENDIF
      ENDIF
16  CONTINUE
15  CONTINUE
      ENDIF

```

C Assign a numerical value for the drop velocity calculations.

```

      IF(DIR.EQ.'U') THEN
      IDir=1
      ELSEIF(DIR.EQ.'D') THEN
      IDir=-1
      ELSE
      IDir=0
      ENDIF

```

C Initialize:

C Number of differential Equations to be solved,
 C IDRY, stores when a dry sorbent particle injected into a prehumidified
 C duct has reached the duct temperature
 C ICOUNT, a counting variable used in the runge kutta routine,
 C Slurry Concentration,
 C Time for the duct gases, and
 C IMIN, the smallest drop not evaporated.
 C NSTEPS, the number of times Rungekutt is called, used to calculate
 C a running average drop temperature which is used to determine
 C when a slurry droplet has dried.

```

      NE=7
      IDRY=0
      ICOUNT=5
      SluConc=0
      Time=0
      IMIN=1
      NSTEPS=0
      IAT=0

```

C Calculate value of following variables and constants:

C CO2, the dry CO2 molar fraction,
 C MWGO, the molecular weight of the duct gas,
 C YO, the initial molar fraction of SO2 in the duct gases,
 C SMFO, the sorbent mass flux in the duct,
 C MolWt, the molecular weight of the sorbent,
 C SD, the sorbent density, gm/m3,
 C VolMol, the molar volume of the sorbent.
 C RoughK, roughness factor to account for the loss of BET surface area
 C as the reaction proceeds.

C ASat, approach to saturation for dry sorbent/condensation case.

```
IF(SurfArea.EQ.0) SurfArea=15
CO2=CO20/(1-DHum)
MWGO=(1-CO2)*29+CO2*44
YO=PPM*1E-6
SMFO=GasMassRate*1000/(MWGO*(1-DHum)+DHum*18)*YO*CaS
IF(SorbType.EQ.'DHYD'.OR.SorbType.EQ.'CHYD') THEN
  MolWt=74
  SD=2.2E6
  SMFO=SMFO*74
ELSE
  MolWt=56
  SD=3.3E6*(1-CaUt)+CaUt*2.96E6
  SMFO=SMFO*56*((1-CaUt)+CaUt*136/56)
ENDIF
Volmol=MolWt/SD
RoughK=5*ALOG(SurfArea/6*SD*PDO-1)
ALPHA=5.22E-5/Volmol
IF(PPM.NE.0) THEN
  ReAsh=AshLoad/(AshLoad+SMFO*(1-ReUt)+SMFO*ReUt*129/74)
  RECYCLE=SMFO*(1/(1-PRECYCLE)-1)*(1-ReUt)
  EFFCAS=(SMFO+RECYCLE)/SMFO*CaS
  UTO=PRECYCLE*ReUt
  ASHREMASS=RECYCLE*(1+ReUt/(1-ReUt)*129/74)*(ReAsh/(1-ReAsh))
  ASHFLUX0=(AshLoad+ASHREMASS)/DuctArea
ENDIF

IF(Slu.EQ.'D'.AND.PRECYCLE.NE.0) THEN
  WF(1)=SMFO/(SMFO+RECYCLE/(1-ReUt))
  WF(2)=RECYCLE/(1-ReUt)/(SMFO+RECYCLE/(1-ReUt))
ENDIF

IF(Slu.EQ.'D') THEN
  TSat=46.13+3816.44/(18.3036-ALOG(DHum*P*760))
  ASat=T0-TSat
ENDIF
```

C Calculate value of following variables:

C GasFlowRate, the duct flow rate, m3/sec,

C GV, the duct gas velocity.

C DropDen0, the initial density of the drop, gm/m3,

C dry AirMassFlux, gm/m2,

C WVMFlux0, the initial water vapor mass flux, gm/m2, and

C SO2MFO, the initial molar flux of SO2.

```
GasFlowRate=GasMassRate*8.206E-2*T0/P/((1-DHum-CO20)*29+
& DHum*18+CO20*44)
GV=GasFlowRate/DuctArea
IF(WaterVel.LT.GV) WaterVel=GV
IF(WaterVel.EQ.GV) THEN
  DelV0=1
ELSE
  DelV0=WaterVel-GV
```

```

ENDIF
IF(Slu.NE.'D') DropDen0=1E6
DUM=GasFlowRate*P/8.206E-5/T0/DuctArea
AirMassFlux=DUM*MWGO*(1-DHum-PPM*1E-6)
WVMFlux0=DHum*18*DUM
SO2MFO=DUM*PPM*1E-6

```

```

C For the slurry spray case calculate:
C SluConc, the slurry concentration including recycle,
C VolFrac, the fraction of the slurry drop occupied by sorbent including
C   recycle,
C WVFrac, the volume fraction of water in drop, and
C ASHVFrac, the volume fraction of ash from recycled ash in drop.

```

```

CASO3=0
SluConc=0
VolFrac=0
ASHVFrac=0
SolidFrac=0
WVFrac=1
IF(Slu.EQ.'S'.AND.PPM.NE.0) THEN
  CASO3=RECYCLE*ReUt/(1-ReUt)*129/74
  SluConc=(SMFO+RECYCLE)/(SMFO+WMRO+RECYCLE+ASHREMASS+CASO3)
  VolFrac=(SMFO+RECYCLE)/SD
  & /(((SMFO+RECYCLE+ASHREMASS+CASO3)/SD+WMRO/DropDen0)
  WVFrac=WMRO/DropDen0
  & /(((SMFO+RECYCLE+ASHREMASS+CASO3)/SD+WMRO/DropDen0)
  ASHVFrac=ASHREMASS/SD
  & /(((SMFO+RECYCLE+ASHREMASS+CASO3)/SD+WMRO/DropDen0)
  SolidFrac=(SMFO+RECYCLE+ASHREMASS+CASO3)
  & /((SMFO+RECYCLE+ASHREMASS+CASO3+WMRO)
ELSEIF(Slu.EQ.'A') THEN
  WVFrac=1
ENDIF

```

```

C Calculate average sorbent diameter of fresh and recycled sorbent.

```

```

IF(Slu.NE.'D') THEN
  PDD=PDO*(1-PRECYCLE*ReUt)**.3333333
ELSE
  PDD=PDO
ENDIF

```

```

C Initialize the independent drop variables:
C VAR(1,1)=Gas Temperature,
C VAR(2,1)=Number of sorbent particles in a drop,
C VAR(3,1)=Number of ash particles in a droplet
C VAR(4,1)=Individual Drop Velocity,
C VAR(5,1)=Mass water remaining in drop,
C VAR(6,1)=Individual Drop temperature,

```

```

C and the dependent drop variables:
C DropNFlux(I), the number flux of drops of each size, #/m2,
C CDO(I), the initial mass of water in a drop,

```


C IVSTOP(I), to remember when a drop has decelerated.
 C DsSolids(I), mass of dissolved solids in a drop.
 C NShell(I), number of radial shells considered in a drop.
 C NStart(I), radial shell from where the initial SO2 concentration will
 C be solved.
 C Tave, running average drop temperature which is used to determine
 C when a slurry droplet has dried.

```

VAR(1,1)=1
DO 30,I=1,NW

```

```

IF(Slu.NE.'D') THEN
  NSHELL(I)=DropDiam(I)/PDD/2+.9
  IF(NSHELL(I).GT.49) NSHELL(I)=49
  IF(NSHELL(I).LT.2) NSHELL(I)=2
  Mevap(I)=NSHELL(I)
  delR=DropDiam(I)/NSHELL(I)/2
  Tave(I)=0
  DO 31,M=1,NSHELL(I)
    Rdry0(I,M)=0
    PD(I,M)=PDD
    PDOLD(I,M)=PD(I,M)
    dR(I,M)=delR
    ShellFlux(I,M)=0
    IF(Slu.EQ.'S') THEN
      NPart(I,M)=8.*((M*delR)**3-((M-1)*delR)**3)
      NASH(I,M)=NPart(I,M)*ASHVFrac/DASH**3
      NPart(I,M)=NPart(I,M)*VolFrac/PDD**3/(1-SP)
    ELSE
      NPart(I,M)=0
      NASH(I,M)=0
    ENDIF
31    CONTINUE
  ELSE
    NSHELL(I)=1
    Mevap(I)=1
    dR(I,1)=DropDiam(1)/2
    PD(I,1)=PDD
    IF(PRECYCLE.NE.0.AND.I.EQ.2) PD(I,1)=PDO*(1-ReUt)**.333333333
    PDRO=PDO*(1-ReUt)**.333333333
    NPart(I,1)=1
  ENDIF

  IF(Slu.NE.'D') THEN
    DropNFlux(I)=6./3.14159*WMRO*WF(I)/DropDen0/
    & DropDiam(I)**3/DuctArea/WVFrac
  ELSE
    IF(I.EQ.1) THEN
      DropNFlux(I)=6./3.14159*SMFO/SD/(1-SP)/PDD**3/DuctArea
    ELSE
      DropNFlux(I)=DropNFlux(1)*PRECYCLE/(1-PRECYCLE)
    ENDIF
  ENDIF

```

```

IF(Slu.EQ.'S') THEN
  CDO(I)=3.14159*DropDiam(I)**3/6*DropDen0*WVFrac
  DsSolids(I)=500E-6*CDO(I)
  VAR(5,I)=1
  VAR(2,I)=DropDiam(I)**3*VolFrac/PDD**3
ELSEIF(Slu.EQ.'D') THEN
  CDO(I)=3.14159*PDO**3/6*SD*(1-SP)
  VAR(5,I)=1E-10
  DsSolids(I)=500E-6*CDO(I)*1E-10
  VAR(2,I)=1
ELSE
  CDO(I)=3.14159*DropDiam(I)**3/6*DropDen0
  VAR(5,I)=1
  VAR(2,I)=0
ENDIF
IF(Slu.NE.'S') THEN
  VAR(3,I)=0
  NASHOLD(I)=0
ELSE
  VAR(3,I)=DropDiam(I)**3*ASHVFrac/DASH**3
  NASHOLD(I)=VAR(3,I)
ENDIF
NPold(I)=VAR(2,I)
NPartOld(I)=VAR(2,I)

IF(Slu.EQ.'D') THEN
  VAR(4,I)=GV
ELSEIF(DAVE.EQ.'N') THEN
  VAR(4,I)=WaterVel
ENDIF

IF(VAR(4,I)-GV.LT..05) THEN
  VAR(4,I)=GV
  IVSTOP(I)=1
ELSE
  IVSTOP(I)=0
ENDIF

VAR(6,I)=DropTemp/T0

```

30 CONTINUE

C Calculate the approximate starting shell for the SO2 profile calculations

```

IF(Slu.NE.'D'.AND.SO2MFO.NE.0.AND.CAS.NE.0) THEN
  DO 50,J=1,NW
    CCa0(J)=.95*(16550/DropTemp-35.62)
    IF(Slu.EQ.'A') CCa0(J)=.95*(16550/325-35.62)
    CMTSO2=(2+.6*SQRT(DropDiam(J)*(VAR(4,J)-GV)/.018E-3))*6.6E-4/
    & DropDiam(J)
    Rough=1+EXP(Roughk*.2)
    BETA=6.28319*PDO*.113E-8
    GAMMA=3.14159*PDO**2*Rough*DissRate
    RATE=20.48*VAR(2,J)*6/3.14159/DropDiam(J)**3/
  50 CONTINUE

```

```

&          (1/GAMMA+1/BETA)
b1=rate*dropdiam(J)/6
b2=cmtso2*Y0
b3=.8e-3*(-cmtso2)
b=(b1-b2)/b3
CO(J)=B-RATE*DropDiam(J)**2/24/.19E-8
IF(CO(J).GT.0) THEN
  RO=.03*DropDiam(J)
  CO(J)=0
ELSE
  RO=.8*SQR((DropDiam(J)**2/4-B*6*.19E-8/RATE))
  CO(J)=0
  IF(RO.GT.DropDiam(J)) RO=.9*DropDiam(J)
ENDIF
dRSO2(J)=DropDiam(J)/2-RO
50  Rold1(J)=0
ELSE
  NStart(1)=1
ENDIF
SMFO=(SMFO+RECYCLE)/DuctArea

```

C Print input data.

```

21  IF(III.GT.1) PRINT 21
    FORMAT(1H1)
    PRINT *
    PRINT *, '          Input file=',FILEIN

```

C Print input sulfur capture parameters.

```

IF(CaS.NE.0.AND.PPM.NE.0) THEN
  PRINT *
  PRINT 55, 'Sorbent Diameter =', PDO*1e6, ' microns'
  PRINT 55, 'Sorbent Surf Area=', SurfArea, ' m2/g '
  PRINT 55, 'Ca/S          =', CaS
  IF(PRECYCLE.NE.0) THEN
    PRINT 55, 'Effective Ca/S   =', EFFCAS, ' (Due to recycle,'
    &, ' calculated)'
    PRINT 55, 'Initial Ave.Util.=', UTO*100, ' % (Due to recycle,'
    &, ' calculated)'
  ENDIF
  IF(Slu.NE.'S') THEN
    PRINT 55, 'Sorbent Mass Rate=', SMFO*DuctArea, ' g/sec (calculated)'
  ELSE
    PRINT 55, 'Slurry Conc.      =', SluConc*100, ' % Wt. (sorbent'
    &, ' only, calculated)'
  ENDIF
ENDIF

IF(PPM.NE.0) THEN
  PRINT 55, 'SO2 Concentration=', PPM, ' ppm '
ENDIF

ENDIF

```

C Print recycle variables.

```

IF(RECYCLE.GT.0) THEN
PRINT 55,'Recycle      =',PRECYCLE*100,' % Wt. of Duct Output'
PRINT 55,'Util. of Recycle =',ReUt*100,' %'
IF(Slu.NE.'D') THEN
PRINT 55,'Ash in Recycle  =',ReAsh*100,' % Wt. (calculated)'
ENDIF
IF(Slu.EQ.'S') THEN
PRINT 55,'Total Solids Conc=',SolidFrac*100,' % Wt. (calculated)'
ENDIF
ENDIF

```

C Print ash properties

```

IF(ASHFLUX0.NE.0.AND.Slu.NE.'D') THEN
PRINT 55,'Ave. Ash Diameter=',DASH*1E6,' microns'
PRINT 55,'Ash Mass Rate   =',ASHLOAD,' g/sec'
ENDIF

```

C Print input humidification parameters.

```

IF(GasMassRate.GT.1) THEN
PRINT 55,'Gas Mass Rate      =',GasMassRate,' Kg/sec '
ELSEIF(GasMassRate.GT..001) THEN
PRINT 55,'Gas Mass Rate      =',GasMassRate*1000,' g/sec '
ELSE
PRINT 55,'Gas Mass Rate      =',GasMassRate*1E6,' mg/sec '
ENDIF
PRINT 55,'Gas Temperature   =',T0,' K '
PRINT 55,'Gas Humidity       =',DHum*100,' % '
PRINT 55,'Gas CO2 Conc.      =',CO20*100,' % '
IF(DuctArea.GT..1) THEN
PRINT 55,'Duct Area          =',DuctArea,' m2 '
ELSE
PRINT 55,'Duct Area          =',DuctArea*1E4,' cm2 '
ENDIF
PRINT 55,'Duct Length        =',DuctLength,' m '
IF(Slu.EQ.'D') PRINT 55,'App. To Sat.      =',ASat,' K (calc.)'
IF(Slu.NE.'D') THEN
IF(WMRO.GT.1) THEN
PRINT 55,'Water Mass Rate   =',WMRO,' g/sec '
ELSE
PRINT 55,'Water Mass Rate   =',WMRO*1000,' mg/sec '
ENDIF
PRINT 55,'Water Velocity    =',WaterVel,' m/sec '
ENDIF
55  FORMAT(15X,A18,F8.2,A,A)

```

```

IF(DIR.EQ.'U') THEN
PRINT *,'          Gas flow direction is up'
ELSEIF(DIR.EQ.'D') THEN
PRINT *,'          Gas flow direction is down'
ELSE

```

```

      PRINT *, '          Gas flow direction is horizontal'
    ENDIF

    IF(DAVE.EQ.'Y') THEN
      PRINT *, '          in Daves Reactor'
    ENDIF

    IF(Slu.NE.'D') THEN
      PRINT *
      PRINT *, '          Drop Size Distribution:'
      PRINT *
      IF(DAVE.EQ.'N') THEN
        PRINT *, '          Drop Diameter          Weight'
        PRINT *, '          (Microns)          Fraction'
        DO 500, I=1, NW
500   PRINT 90, DropDiam(I)*1E6, WF(I)
        ELSE
          PRINT *, '          Drop Diameter          Weight          ',
          &' Drop'
          PRINT *, '          (Microns)          Fraction          ',
          &' Velocity'
          DO 501, I=1, NW
501   PRINT 91, DropDiam(I)*1E6, WF(I), VAR(4, I)
        ENDIF
      ENDIF

90   FORMAT(18X, F6.1, 15X, F6.3)
91   FORMAT(16X, F6.1, 13X, F6.3, 10X, F6.1)
      PRINT *

```

C Print results heading.

```

      CALL HEADING()

```

```

      RETURN
    END

```

SUBROUTINE CHK(HMIN,Dist,VAR)

C Assign appropriate step size values to each drop size.

```
REAL *8 HMIN,Dist
REAL DropDiam(15),VAR(7,15)
INTEGER ISTOP(15)
CHARACTER *1 Slu

COMMON/I/ISTOP
COMMON/IMIN/IMIN
COMMON/RKPR/NW,NE
COMMON/PRNT/GV
COMMON/DROP/DropDiam
COMMON/SLU/Slu

IF(ISTOP(NW).EQ.1) THEN
    HMIN=2D-2
    GO TO 101
ELSEIF(Slu.EQ.'D') THEN
    HMIN=1D-4
    GO TO 101
ENDIF

DO 100,I=1,NW

IF(ISTOP(I).EQ.1) GO TO 100
IF(DropDiam(I).LE.9E-6) THEN
    HMIN=1D-3
ELSEIF(DropDiam(I).LE.12E-6) THEN
    HMIN=2D-3
ELSEIF(DropDiam(I).LE.24E-6) THEN
    HMIN=1D-2
ELSEIF(DropDiam(I).LE.42E-6) THEN
    HMIN=2D-2
ELSEIF(DropDiam(I).LE.64E-6) THEN
    HMIN=1D-1
ELSEIF(DropDiam(I).LE.84E-6) THEN
    HMIN=2D-1
ELSE
    HMIN=5D-1
ENDIF
IF(VAR(5,I).GE.1) HMIN=HMIN/10
IF(GV.LT.1) HMIN=HMIN*3
IF(GV.LT.8.1.AND.VAR(4,I).LT.8) HMIN=HMIN/INT(16/VAR(4,I))
IF(GV.GT.23) HMIN=HMIN*INT(VAR(4,I)/12)
GO TO 101
100 CONTINUE

101 IF(GV.LT.8.1.AND.VAR(4,I).LT.8) HMIN=HMIN/INT(16/VAR(4,I))
    IF(GV.GT.23) HMIN=HMIN*INT(VAR(4,I)/12)
    IF(Dist.LT.2D-1-1D-5.AND.HMIN.GT.1D-2) HMIN=1D-2
```

IF(Dist.GT..1-1D-5.AND.Dist.LE.1-1D-4.AND.HMIN.GT.1D-1)HMIN=1D-1
IF(Dist.GT.1.AND.HMIN.GT.2D-1) HMIN=2D-1

RETURN
END

SUBROUTINE RUNGKUTT(VAR,PD,Dist,HMIN,IWARN)

C Perform 4th order Runge Kutta on the differential equations. Each
C drop size has an individual step size and calculations are performed
C only when appropriate.

REAL K(4,7,15),VAR(7,15),W(7,15),CD0(15),MWGO,NASH(15,50)
REAL NPartOld(15),DropNFlux(15),DropDiam(15),DTime(15),PD(15,50)
REAL KPD(4,15,50),WPD(15,50),dR(15,50),NPart(15,50),Tave(15)
REAL NPolD(15,50),NASHOLD(15),XW(15)
REAL *8 Dist,Hmin
INTEGER ISTOP(15),Iold(15),IVSTOP(15)
INTEGER NSHELL(15),NStart(15),Mevap(15)
CHARACTER *1 Slu

COMMON/FN/DropNFlux,DuctArea,AirMassFlux,WVMFlux0
COMMON/PP/P
COMMON/DROP/DropDiam
COMMON/DUM/W,WPD
COMMON/IMIN/IMIN
COMMON/RKPR/NW,NE
COMMON/I/ISTOP
COMMON/PRNT/GV
COMMON/Iold/Iold
COMMON/P/CD0,SMF0
COMMON/Y/SO2MF0
COMMON/CAS/CaS
COMMON/E/SD,PDO,SP,PDD
COMMON/T/Time
COMMON/CO2/CO2,MWGO
COMMON/SLU/Slu
COMMON/DTIME/DTime
COMMON/TO/TO
COMMON>IDRY/IDRY
COMMON/IC/ICOUNT
COMMON/C/IVSTOP
COMMON/NP/NPartOld
COMMON/NS/NSHELL
COMMON/NT/NStart
COMMON/DR/dR
COMMON/NPDR/NPart
COMMON/MEVAP/Mevap
COMMON/TAVE/Tave,NSTEPS
COMMON/DV/DeIVO
COMMON/ICE/ICEASE
COMMON/NASH/NASH
COMMON/NAOLD/NASHOLD
COMMON/IAT/IAT

C Determine on which drop sizes calculations are to be performed and
C calculate Water Vapor Mass Flux, and Gas Velocity.

ICOUNT=ICOUNT+1


```

WVMFlux=WVMFlux0

ITEST=1
DO 899,J=1,NW

IF(ISTOP(J).EQ.1.AND.SO2MFO.EQ.0) THEN
    IMIN=J+1
ELSEIF(ISTOP(J).EQ.1) THEN
    VAR(6,J)=VAR(1,1)
ENDIF

IF(IVSTOP(J).EQ.0.OR.XW(J).GE.1) ITEST=0

C If condensation has stopped reset step size.

IF(XW(J).GE.1.AND.VAR(5,J).LT.1) CALL CHK(HMIN,Dist,VAR)
XW(J)=VAR(5,J)

899  WVMFlux=WVMFlux+DropNFlux(J)*CDO(J)*(1-VAR(5,J))

C Incrementally increase step size.

IF(Slu.EQ.'S') ITEST=1
IF(Slu.EQ.'D') ITEST=0
IF(ITEST.EQ.1) THEN
    HMIN=1.03*HMIN
    IF(Dist.LT..1-1D-4.AND.HMIN.GT..005) HMIN=.005
    IF(Dist.LT.1-1E-3.AND.HMIN.GT..02) HMIN=.02
ENDIF

IF(Slu.EQ.'D') WVMFlux=WVMFlux0-CDO(1)*VAR(5,1)*DropNFlux(1)
GV=(AirMassFlux/MWGO+WVMFlux/18)/(P/8.206E-5/VAR(1,1)/T0)
GVold=GV

C Initialize the dummy variable.

9    DO 10,I=1,NE
    DO 20,J=1,NW
    IF(I.EQ.7) THEN
        DO 15,M=1,NSHELL(J)
15    WPD(J,M)=PD(J,M)
    ELSE
        W(I,J)=VAR(I,J)
    ENDIF
    IF(I.EQ.1) GO TO 10
20    CONTINUE
10    CONTINUE

C Perform Runge Kutta calculations.
C Evaporation from all drops contributes to the change in the duct gas
C   temperature, VAR(1,1).
C For the dry sorbent injection case don't calculate the differential
C   equations for sorbent capture and particle deceleration.
C For the slurry spray case don't calculate the differential equation

```

C for sorbent capture.
 C If the drop temperature of the smallest evaporating drop becomes
 C unstable (changes by more than one degree Kelvin in one step)
 C reduce step size.

```

IF(IAT.EQ.7) IAT=0
IAT=IAT+1
DO 55,L=1,4
IT=0
IF(L.EQ.1.AND.IAT.EQ.1) IT=1

```

C Calculate K's.

```

DO 40,J=IMIN,NW
DO 50,I=1,NE
IF(I.EQ.7.AND.SO2MFO.NE.0.AND.CaS.NE.0) THEN
DO 45,M=NShell(J),1,-1
IF(W(4,J)-GV.GT..4*DeIV0.AND.M.NE.NShell(J)) THEN
KPD(L,J,M)=KPD(L,J,NShell(J))
ELSE
KPD(L,J,M)=HMIN*FNC(IT,I,J,M)
ENDIF
CONTINUE
45 ELSE
K(L,I,J)=HMIN*FNC(IT,I,J,0)
IF(ICEASE.EQ.1) RETURN
ENDIF
IF(ISTOP(J).EQ.1.AND.SO2MFO.EQ.0) GO TO 40
50 CONTINUE
40 CONTINUE

```

C Calculate new dummy variable value.

```

IF(L.EQ.4) GO TO 100
DO 60,I=1,NE
IF(Slu.EQ.'D') THEN
IF(I.EQ.2.OR.I.EQ.3.OR.I.EQ.4) GO TO 60
IF(W(1,1).EQ.W(6,J).AND.I.EQ.6) GO TO 60
ENDIF
IF(Slu.EQ.'S'.AND.I.EQ.2) GO TO 60
DO 70,J=IMIN,NW
IF(I.EQ.1) THEN
JJ=1
ELSE
JJ=J
ENDIF
IF(I.EQ.7.AND.SO2MFO.NE.0.AND.CaS.NE.0) THEN
DO 65,M=1,NSHELL(J)
IF(L.NE.3) THEN

```

```

        DUM=PD(J,M)+KPD(L,J,M)/2
    ELSE
        DUM=PD(J,M)+KPD(L,J,M)
    ENDIF
    WPD(J,M)=DUM
    IF(WPD(J,M).LT.1E-3*PDO) WPD(J,M)=0
65    CONTINUE
ELSE
    IF(L.NE.3) THEN
        DUM=VAR(I,JJ)+K(L,I,J)/2
    ELSE
        DUM=VAR(I,JJ)+K(L,I,J)
    ENDIF
    IF(I.EQ.6.AND.ICOUNT.GT.5.AND.
&      ABS(DUM-VAR(6,JJ)).GT..5/TO.AND.Slu.NE.'D') GO TO 131
    IF(I.EQ.4.AND.DUM.LT.0) GO TO 131
    W(I,JJ)=DUM
    ENDIF

70    CONTINUE
60    CONTINUE

55    CONTINUE

C Calculate new variable value.

100    DO 150,I=1,NE
        IF(Slu.EQ.'D') THEN
            IF(I.EQ.2.OR.I.EQ.3.OR.I.EQ.4) GO TO 150
            IF(I.EQ.6.AND.(VAR(1,1)-VAR(6,1)).LT..1/TO) THEN
                VAR(6,1)=VAR(1,1)
                GO TO 150
            ENDIF
        ENDIF
        IF(Slu.EQ.'S'.AND.I.EQ.2) GO TO 150

        DO 160,J=IMIN,NW

            IF(I.EQ.1) THEN
                JJ=1
            ELSE
                JJ=J
            ENDIF

            IF(I.EQ.7.AND.SO2MFO.NE.0) THEN
                DO 155,M=1,NSHELL(J)
                    PD(J,M)=PD(J,M)+(KPD(1,J,M)+2*KPD(2,J,M)+
&      2*KPD(3,J,M)+KPD(4,J,M))/6
                    IF(PD(J,M).LT.1E-3*PDO) PD(J,M)=0
155    CONTINUE
                ELSE
                    DUM=VAR(I,JJ)+(K(1,I,J)+2*K(2,I,J)+2*K(3,I,J)+K(4,I,J))/6
                    IF(Slu.EQ.'D'.AND.IDRY.EQ.0.AND.VAR(5,1).GE.DUM.AND.I.EQ.5) THEN

```

```

        IDRY=1
        GO TO 160
    ENDIF
    IF(I.EQ.4.AND.DUM.LT.0) GO TO 131

```

```

    VAR(I,JJ)=DUM

```

```

ENDIF

```

C If variable is outside normal ranges default program.

```

    IF(VAR(I,JJ).LT.0.OR.VAR(I,JJ).GT.1000.AND.I.NE.2) THEN
        IF(S1u.NE.'D') THEN
            IWARN=3
        ELSE
            IWARN=6
        ENDIF
        RETURN
    ENDIF

```

```

160    CONTINUE

```

```

150    CONTINUE

```

C Calculate the change in the number of sorbent particles in each shell
 C due to diffusion of the particles.

```

    IF(S1u.NE.'D'.AND.SO2MF0.NE.0.AND.CAS.NE.0.AND.VAR(2,J).NE.0)
    &    THEN
        CALL PDIF(HMIN,VAR,PD)

```

C If an outer radial shell is too small, combine it with the next one in.

```

    DO 285,J=1,NW
        IF(MEVAP(J).GT.0) THEN
            DO 286,M=NShell(J),Mevap(J),-1
                IF(dR(J,M).LE..001E-6) THEN
                    IF(M.NE.NShell(J)) THEN
                        PD(J,M)=(PD(J,M)*NPart(J,M)+PD(J,M+1)*NPart(J,M+1))
                        &    /(NPart(J,M)+NPart(J,M+1))
                        NPart(J,M)=NPart(J,M)+NPart(J,M+1)
                        NASH(J,M)=NASH(J,M)+NASH(J,M+1)
                        DO 287,MM=M+1,NShell(J)-1
                            NPart(J,MM)=NPart(J,MM+1)
                            NASH(J,MM)=NASH(J,MM+1)
                            PD(J,MM)=PD(J,MM+1)
                        287
                    ELSE
                        PD(J,M-1)=(PD(J,M)*NPart(J,M)+PD(J,M-1)*NPart(J,M-1))
                        &    /(NPart(J,M)+NPart(J,M-1))
                        NPart(J,M-1)=NPart(J,M)+NPart(J,M-1)
                        NASH(J,M-1)=NASH(J,M)+NASH(J,M-1)
                        Mevap(J)=Mevap(J)-1
                    ENDIF
                    NShell(J)=NShell(J)-1
                ENDIF
            ENDIF
        ENDIF
    ENDIF

```

```

286     CONTINUE
      ENDIF
285     CONTINUE
      ENDIF

      Time=Time+Hmin/(GV+GVOld)*2

      DO 290,J=1,NW

C If IVSTOP(J) equals 1 set the drop velocity equal to the gas velocity.
      IF(IVSTOP(J).EQ.1.AND.SO2MF0.NE.0) VAR(4,J)=GV

C Calculate an average particle diameter in each drop size for the
C   scavenging case.
      IF(Slu.NE.'S'.AND.SO2MF0.NE.0.AND.J.GE.IMIN.AND.VAR(4,J)-GV.GT.
&      .9*DeIVO.AND.Slu.NE.'D') THEN
          M=1
          PD(J,M)=((NPolD(J,M)*PD(J,M)**3+(NPart(J,M)-NPolD(J,M))*
&      PDD**3)/NPart(J,M))**.33333333
          DO 295,M=1,NSHELL(J)
              PD(J,M)=PD(J,1)
295      NPolD(J,M)=NPart(J,M)
          ENDIF
          NPartOld(J)=VAR(2,J)
          NASHOLD(J)=VAR(3,J)

C Calculate the drop time in the duct.
      IF(IoId(J).EQ.0.OR.SO2MF0.NE.0.and.istop(J).eq.0) DTime(J)=
&      DTime(J)+HMIN/VAR(4,J)

C If evaporation has ceased set the final mass of water in VAR(5,J),
C   call CHK to find the new step size, and set the K's to zero.
      IF(IoId(J).NE.ISTOP(J).AND.Slu.NE.'D') THEN
          CALL CHK(HMIN,Dist,VAR)
          ICOUNT=5

          DO 200,I=1,NE
              DO 210,L=1,4
                  IF(I.EQ.7.AND.SO2MF0.NE.0) THEN
                      DO 205,M=1,NSHELL(J)
205      KPD(L,J,M)=0
                  ELSE
                      K(L,I,J)=0
                  ENDIF
              CONTINUE
210      CONTINUE
200      CONTINUE

          ENDIF

```

290 Iold(J)=ISTOP(J)

C If evaporation has ceased, stop evaporation calculations.

```
      NSTEPS=NSTEPS+1
      DO 300,J=IMIN,NW
      Tave(J)=(Tave(J)*NSTEPS+VAR(6,1))/NSTEPS+1
300   IF(VAR(6,1).GT..3*(VAR(1,1)-Tave(J))+Tave(J).AND.VAR(5,1).LT..1
      &.AND.Slu.NE.'D'.AND.VAR(1,1)-VAR(6,NW).GT..1/TO) ISTOP(J)=1
```

C Send message to main program when evaporation of all drops has ceased.

```
      IF(ISTOP(NW).EQ.1.AND.SO2MF0.EQ.0) IWARN=4
```

C Call FITE subroutine to calculate the solids volume in each radial shell.

```
      IF(Slu.NE.'D') CALL FITE(PD)
```

```
      RETURN
```

C If variable is diverging, reduce the step size.

```
131  HMIN=HMIN/SQRT(10.)
      IF(HMIN.LT.1D-8) THEN
          IWARN=2
          print *, 'w(1,1)= ', w(1,1), ' imin= ', imin
          print *, 'var(6,imin)= ', var(6,imin), ' w(6,imin)= ', w(6,imin)
          print *, 'var(1,1)= ', var(1,1)
          print *, 'pd(' , j, m, ')=' , pd(j, m), ' dum=' , dum
          print *, 'wpd(' , j, m, ')=' , wpd(j, m), ' dum=' , dum
          RETURN
      ENDIF
      ICOUNT=0
      GO TO 9

      END
```

SUBROUTINE PDIF(HMIN,VAR,PD)

C Calculate the change in the number of particles from shell to shell
C due to diffusion of the particles.

REAL VAR(7,15),PD(15,50),dR(15,50),NPart(15,50),DropDiam(15)
REAL *8 HMIN
INTEGER Mevap(15),NShell(15)

COMMON/DR/dR
COMMON/NPDR/NPart
COMMON/RKPR/NW,NE
COMMON/MEVAP/Mevap
COMMON/DROP/DropDiam
COMMON/NS/NShell
COMMON/TO/TO
common/dis/dis

N=HMIN/.001
IF(N.LT.1) N=1
H=HMIN/N
DO 10,J=1,NW
IF(Mevap(J).EQ.0.OR.VAR(2,J).EQ.0) GO TO 10
DIFFPARTO=6.782E-35*(TO*VAR(6,J))**6.416

DO 100,I=1,N
R=DropDiam(J)/2

IF(Mevap(J).EQ.NShell(J)) THEN
ME=NShell(J)
ELSE
ME=Mevap(J)+1
ENDIF

DO 20,M=ME,2,-1

IF(PD(J,M).LT.1E-10) GO TO 20
DIFFPART=DIFFPARTO/PD(J,M)
R=R-dR(J,M)
C1=NPart(J,M)/((R+dR(J,M))**3-R**3)
C0=NPart(J,M-1)/(R**3-(R-dR(J,M-1))**3)
DRBAR=(dR(J,M)+dR(J,M-1))/2
dN=3*R**2*DIFFPART*(C1-C0)/DRBAR*H/VAR(4,J)
IF(dN.GT.NPart(J,M)) dN=.9*NPart(J,M)
NPart(J,M)=NPart(J,M)-dN
IF(dN.GT.0) THEN
PD(J,M-1)=((PD(J,M)**3*(dN)+PD(J,M-1)**3*NPart(J,M-1))
& /((dN+NPart(J,M-1))**3.33333333
ELSE
PD(J,M)=((PD(J,M-1)**3*(-dN)+PD(J,M)**3*NPart(J,M))
& /((-dN+NPart(J,M))**3.33333333
ENDIF
NPart(J,M-1)=NPart(J,M-1)+dN
20 CONTINUE

100 CONTINUE
10 CONTINUE

RETURN
END


```

SUBROUTINE FITE(PD)

REAL DropDiam(15),dR(15,50),PD(15,50),PDOLD(15,50)
REAL VSULFITE(15,50),NPart(15,50),RFRONT(15)
INTEGER NSHELL(15),ISTOP(15)

COMMON/DROP/DropDiam
COMMON/DR/dR
COMMON/NS/NSHELL
COMMON/I/ISTOP
COMMON/RKPR/NW,NE
COMMON/NPDR/NPart
COMMON/RF/RFRONT
COMMON/VS/VSULFITE
COMMON/A/ALPHA
COMMON/PDOLD/PDOLD

DO 100,J=1,NW
  IF(ISTOP(J).EQ.1) GO TO 100
  R=0
  SUM=0
  DO 200,M=1,NSHELL(J)
    R=R+dR(J,M)
    IF(R-dR(J,M).LE.RFRONT(J).AND.R.GE.RFRONT(J)) THEN
      VSULFITE(J,M)=VSULFITE(J,M)+SUM+.5236*(PDOLD(J,M)**3-
&      PD(J,M)**3)*ALPHA*NPart(J,M)
    ELSEIF(R.LT.RFRONT(J)) THEN
      SUM=SUM+.5236*(PDOLD(J,M)**3-PD(J,M)**3)*ALPHA*NPart(J,M)
    ELSE
      VSULFITE(J,M)=VSULFITE(J,M)+.5236*(PDOLD(J,M)**3-PD(J,M)**3)*
&      ALPHA*NPart(J,M)
    ENDIF
    200 PDOLD(J,M)=PD(J,M)
  100 CONTINUE

  RETURN
END

```

FUNCTION FNC(IT,I,J,M)

C Calculate the values of the differential equations.

C W(1,1)=Gas Temperature

C W(2,J)=Number of sorbent particles in a drop

C W(3,J)=Number of ash particles in a drop

C W(4,J)=Individual Drop Velocity

C W(5,J)=Mass water remaining in drop

C W(6,J)=Individual Drop Temperature

C WPD(J,M)=Sorbent diameter in drop, function of radial position

REAL CDO(15),DropNFlux(15),DropDiam(15)

REAL W(7,15),WPD(15,50)

INTEGER ISTOP(15),IVSTOP(15)

CHARACTER *1 Slu

COMMON/DUM/W, WPD

COMMON/FN/DropNFlux,DuctArea,AirMassFlux,WVMFlux0

COMMON/DROP/DropDiam

COMMON/I/ISTOP

COMMON/C/IVSTOP

COMMON/E/SD,PDO,SP,PDD

COMMON/P/CDO,SMFO

COMMON/PRNT/GV

COMMON/VOL/VolMol,CaUt

COMMON/Y/SO2MFO

COMMON/CAS/CaS

COMMON/DIR/IDir

COMMON/SLU/Slu

COMMON/TO/TO

COMMON/IDRY/IDRY

COMMON/DV/DeIVO

COMMON/ICE/ICEASE

COMMON/ASH/ASHFLUX0,DASH,ASHFLUX

common/dis/dis

GO TO (1,2,3,4,5,6,7),I

C Calculate physical constants, size of differential shells, and flux
C of SO2 through the droplet (or agglomerate).

1 IF(W(5,J).LT..002.OR.W(6,J).GE..99*W(1,1).AND.W(5,J).LT..03)THEN

IF(Slu.NE.'D') ISTOP(J)=1

ENDIF

IF(ABS(W(4,J)-GV).LT..49) IVSTOP(J)=1

CALL PHY (IT,J,Q,ER,ERate,CpW,WVMFlux,HtCapG,SMF,
& DropDens,Re,DenG,HTVAP,HtCapW)

IF(Slu.NE.'D'.AND.SO2MFO.NE.0.AND.CaS.NE.0.AND.ISTOP(J).NE.1.AND
& .IT.EQ.1.AND.W(2,J).NE.0) THEN

IF(W(4,J)-GV.LE..4*DeIVO.AND.Slu.NE.'S') THEN

CALL FLX(J,-ER,SMF)

```

    ELSEIF(Slu.EQ.'S') THEN
      CALL FLX(J,-ER,SMF)
    ENDIF
    IF(ICEASE.EQ.1) RETURN
  ENDIF

```

C Calculate the gas temperature diff. eqn.

```

    IF(ISTOP(J).EQ.1.OR.IDRY.EQ.1) THEN
      FNC=0
      RETURN
    ENDIF

    FNC=-DropNFlux(J)/W(4,J)*(Q/TO+ERate*CpW*(W(1,1)-W(6,J)))
    &      /(AirMassFlux+WVMFlux)/HtCapG

    RETURN

```

C Calculate the sorbent capture diff. eqn. for an individual drop.

```

2    IF(IVSTOP(J).EQ.1.OR.Slu.EQ.'S'.OR.Slu.EQ.'D') THEN
      FNC=0
    ELSE
      FNC=1.5*DropDiam(J)**2*SMF*ETA(W(4,J),DropDiam(J),SD,PDD)
    &      /PDD**3/SD/(1-SP)/W(4,J)/GV*ABS((W(4,J)-GV))
    ENDIF
    FNC1=FNC

    RETURN

```

C Calculate the ash capture diff. eqn. for an individual drop.

```

3    IF(IVSTOP(J).EQ.1.OR.Slu.EQ.'D'.OR.W(4,J)-GV.LT..5) THEN
      FNC=0
    ELSE
      FNC=1.5*DropDiam(J)**2*ASHFLUX*ETA(W(4,J),DropDiam(J),SD,DASH)
    &      /DASH**3/SD/W(4,J)/GV*ABS((W(4,J)-GV))
    ENDIF
    FNC2=FNC

    RETURN

```

C Calculate individual drop deceleration diff. eqn.

```

4    IF(IVSTOP(J).EQ.1.OR.Slu.EQ.'D') THEN
      FNC=0
    ELSE

      FNC=-.75*DenG/DropDens/DropDiam(J)/W(4,J)*(W(4,J)-GV)**2*27/
    &      Re**.84-IDir*9.8*(DropDens-DenG)/DropDens/W(4,J)
    &      -3.14159/6*SD*(1-SP)*PDD**3/W(5,J)/CDO(J)*(W(4,J)-GV)*FNC1
    &      -3.14159/6*SD*DASH**3/W(5,J)/CDO(J)*(W(4,J)-GV)*FNC2
    ENDIF
    RETURN

```

C Calculate the drop water mass diff. eqn.

```
5   IF(ISTOP(J).EQ.1) THEN
      FNC=0
    ELSE
      FNC=-ERate*18/W(4,J)/CDO(J)
    ENDIF
```

RETURN

C Calculate the individual drop temperature diff. eqn.

```
6   IF(ISTOP(J).EQ.0) THEN
      FNC=6/3.14159/DropDiam(J)**3*(Q-ERate*HTVAP)/HtCapW/DropDens/
      &      W(4,J)
      FNC=FNC/TO
    ELSE
      FNC=0
    ENDIF
```

RETURN

C Calculate the sorbent utilization rate.

```
7   FNC=0
      IF(W(2,J).EQ.0.OR.SO2MF0.EQ.0) RETURN
```

C Solve sulfur capture differential equation module.

CALL SULF(J,M,FNC,ER)

RETURN
END

```

FUNCTION ETA(U,D,SD,PD)
C Calculate collision efficiency.

IMPLICIT REAL (N)

COMMON/PRNT/GV
COMMON/ET/ReG,VisG

PSI=SD*PD**2*(U-GV)/18/VisG/D

IF(PSI.LT.1./24) THEN
  NIP=0
ELSE
  NIP=4*PSI**2/(2*PSI+.5)**2
ENDIF

IF(PSI.LE..607) THEN
  NIV=0
ELSE
  NIV=1/(1+.75*ALOG(4*PSI)/(2*PSI-1.214))**2
ENDIF

IF(ReG.LE.1) THEN
  NI=NIV
ELSE
  NI=(NIV+NIP*ReG/60)/(1+ReG/60)
ENDIF

R=1+PD/D
NCV=R*R-3./2*R+1./2/R

IF(ReG.LE.1) THEN
  NCP=0
ELSE
  NCP=R**2-1/R
ENDIF

IF((U-GV).EQ.0) THEN
  NC=0
ELSE
  NC=(NCV+NCP*ReG/60)/(1+ReG/60)
ENDIF

ETA=1-(1-NI)*(1-NC)

RETURN
END

```

SUBROUTINE SULF(J,M,FNC,ER)

REAL W(7,15),WPD(15,50),DropDiam(15),NPART(15,50),RWCore(15)
REAL MolWt,KDISSOC,Rdry0(15,50),CDO(15)
REAL ShellFlux(15,50)
INTEGER ISTOP(15)
CHARACTER *1 Slu

COMMON/DUM/W,WPD
COMMON/SLU/Slu
COMMON/E/SD,PDO,SP,PDD
COMMON/P/CDO,SMFO
COMMON/SA/RoughK
COMMON/AG/DissRate,RateK,Dprod
COMMON/DROP/DropDiam
COMMON/VOL/VolMol,CaUt
COMMON/SO2/DSO2,CMTSO2,HE,KDISSOC,DH2SO3,DHSO3,YS8
COMMON/LIME/Dlime,ClimeEq
COMMON/NPDR/NPart
COMMON/MOL/MolWt
COMMON/RW/RWCore
COMMON/RD/Rdry0
COMMON/A/ALPHA
COMMON/CG/Cg
COMMON/SHEL/ShellFlux
COMMON/I/ISTOP
COMMON/PRNT/GV
COMMON/DV/DelV0
COMMON>IDRY/IDRY
COMMON/XW/XW
common/dis/dis

C Calculate the rate of sorbent consumption (dDp/dt) for the case when
C sorbent particle is within the droplet surface (both
C moving and stopped relative to the gas velocity).

IF(ISTOP(J).EQ.0.AND.Slu.NE.'D') THEN

IF(Slu.EQ.'S'.OR.W(4,J)-GV.LT..4*DelV0) THEN

IF(WPD(J,M).EQ.0) THEN

FNC=0

RETURN

ENDIF

IF(M.NE.1) THEN

FNC=-2*VolMol*(ShellFlux(J,M)-ShellFlux(J,M-1))/(1-SP)/
& WPD(J,M)**2/NPart(J,M)

ELSE

FNC=-2*VolMol*ShellFlux(J,M)/(1-SP)/
& WPD(J,M)**2/NPart(J,M)

ENDIF

C Else calculate the rate of sorbent consumption during deceleration.

ELSE

```
Rough=1+EXP(RoughK*((WPD(J,M)/PDO)**3-.8))
U=4*Dlime*ClimeEq/WPD(J,M)**2
V=Dlime/Rough/DissRate
DUM2=1/Rough/DissRate
A1=W(2,J)*ClimeEq*(WPD(J,M)/DropDiam(J))**2
A2=CMTS02*YS8
A3=ER-CMTS02
B1=KDISSOC**2
B2=4*KDISSOC/HE
```

C Iteratively calculate film thickness and therefore XS.

```
XS=0
C=0
DO 20,I=1,10
A=A1/(De1(C,WPD(J,M),U,V,J,M)/DLime+DUM2)
XS=(A-A2)/A3
IF(XS.LT.0) GO TO 21
C=(-KDISSOC+SQRT(B1+B2*XS))/2
IF(ABS(XS-XSOLD).LT..00001*XS) GO TO 21
20 XSOLD=XS

21 IF(XS.LT.0) XS=0
FNC=-2*VolMol*DropDiam(J)**2/((1-SP)/W(2,J)/WPD(J,M)**2*
& (CMTS02*(YS8-XS)+XS*ER)
ENDIF
```

C Else calculate the rate of sorbent consumption (dDp/dt) for the case
C when the water core has receded past a sorbent particle.

ELSEIF(Slu.NE.'D') THEN

```
IF(WPD(J,M).GT.0) THEN
C=Cg*YS8
Rough=1+EXP(RoughK*((WPD(J,M)/PDO)**3-.8))
Rratio=1/(ALPHA*(2*Rdry0(J,M)/WPD(J,M))**3+1-ALPHA)**.33333333
FNC=-VolMol*RateK*Rough*C/(1+RateK*Rough/Dprod*WPD(J,M)/
& 2*(1-Rratio))
ENDIF
```

C Else calculate the rate of sorbent consumption (dDp/dt) for the dry
C sorbent injection case.

ELSE

```
XW=W(5,J)*CDO(J)/(3.14159*PDO**3/6*(1-SP))*VolMol/18
IF(XW.GT..25) THEN
XW=.25
IDRY=1
ENDIF
```

```

Rough=1+EXP(RoughK*((WPD(J,M)/PDO)**3-.8))
RK=RateK*Rough*(XW/.25)
Rs3=(ALPHA*PDO**3+WPD(J,M)**3*(1-ALPHA))/8
Rratio=1/(ALPHA*PDO**3/Rs3+1-ALPHA)**.33333333
FNC=-2*MolWt*YS8*Cg/SD/(1/RK+Rratio**2*Cg
&      /CMTS02+1/Dprod/(XW/.25)*WPD(J,M)*(1-Rratio))

ENDIF

FNC=FNC/W(4,J)
RETURN
END

```



```

SUBROUTINE PHY (IT,J,Q,ER,ERate,CpW,WVMFlux,HtCapG,SMF,
& DropDens,Re,DenG,HTVAP,HtCapW)

```

```

REAL CDO(15),DropNFlux(15),DropDiam(15),Nu,NPart(15,50)
REAL W(7,15),WPD(15,50),NPartOld(15),DsSolids(15),dR(15,50)
REAL KDISSOC,RWCore(15),RdryO(15,50),Dmin(15),VolPart(15,50)
REAL MWF,MWG,MUAIR,MUW,MolWt,MWGO,SolFrac(15,50),NASH(15,50)
REAL NASHOLD(15),VSULFITE(15,50)
INTEGER ISTOP(15),IVSTOP(15),NSHELL(15),Mevap(15),NSTART(15)
INTEGER IFlux(15)
CHARACTER *1 Slu

```

```

COMMON/DUM/W,WPD
COMMON/FN/DropNFlux,DuctArea,AirMassFlux,WVMFluxO
COMMON/DROP/DropDiam
COMMON/PP/P
COMMON/I/ISTOP
COMMON/C/IVSTOP
COMMON/E/SD,PDO,SP,PDD
COMMON/P/CDO,SMFO
COMMON/RKPR/NW,NE
COMMON/PRNT/GV
COMMON/VOL/VolMol,CaUt
COMMON/MOL/MolWt
COMMON/Y/SO2MFO
COMMON/IMIN/IMIN
COMMON/CO2/CO2,MWGO
COMMON/SLU/Slu
COMMON/TO/TO
COMMON/IDRY/IDRY
COMMON/ET/ReG,VisG
COMMON/DS/DsSolids
COMMON/NS/NSHELL
COMMON/DR/dR
COMMON/NPDR/NPart
COMMON/MEVAP/Mevap
COMMON/RW/RWCore
COMMON/SO2/DSO2,CMTSO2,HE,KDISSOC,DH2SO3,DHSO3,YS8
COMMON/LIME/Dlime,ClimeEq
COMMON/RD/RdryO
COMMON/CG/Cg
COMMON/A/ALPHA
COMMON/SA/RoughK
COMMON/NT/NSTART
COMMON/VL/VolPart
COMMON/SOL/SolFrac
COMMON/CAS/CAS
COMMON/NP/NPartOld
COMMON/IF/IFlux
COMMON/ICE/ICEASE
COMMON/DV/DelVO
COMMON/NASH/NASH
COMMON/ASH/ASHFLUXO,DASH,ASHFLUX

```

```

COMMON/NAOLD/NASHOLD
COMMON/UTO/UTO, EFFCAS, PDRO
COMMON/PACK/PACK
COMMON/VS/V SULFITE
common/dis/dis

```

C Calculate gas, film, and drop temperatures.

```

Td=W(6,J)*T0
Tg=W(1,1)*T0
Tf=(Tg+Td)/2
Cf=P/8.206E-5/Tf
Cg=P/8.206E-5/Tg

```

C If the drop has stopped evaporating, calculate its final water content.

```

IF(SMFO.EQ.0.AND.W(5,J).LT.0.001.AND.ISTOP(J).EQ.0.AND.Slu.NE.
& 'D') THEN
  W(5,J)=1E-30
  ISTOP(J)=1
  IF(SO2MFO.EQ.0) IMIN=IMIN+1
ENDIF

```

C Calculate Sorbent Mass Rate, Water Vapor Mass Flux and Gas Velocity.

```

IF(J.EQ.IMIN) THEN
  SMF=SMFO
  ASHFLUX=ASHFLUX0
  WVMFlux=WVMFlux0
  DO 100,L=1,NW
    IF(Slu.NE.'S') SMF=SMF-DropNFlux(L)*W(2,L)*3.14159/6*
& SD*(1-SP)*PDD**3
    IF(Slu.NE.'D'.AND.ASHFLUX0.GT.0) ASHFLUX=ASHFLUX-DropNFlux(L)
& *W(3,L)*3.14159/6*SD*DASH**3
100  WVMFlux=WVMFlux+DropNFlux(L)*CDO(L)*(1-W(5,L))
    IF(Slu.EQ.'D') THEN
      WVMFlux=WVMFlux0
      DO 103,L=1,NW
103  WVMFlux=WVMFlux-CDO(L)*W(5,L)*DropNFlux(L)
      ENDIF
      DenG=P/8.206E-5/Tg
      GV=(AirMassFlux/MWG0+WVMFlux/18)/DenG
      GasMassFlux=WVMFlux+AirMassFlux
      YG=WVMFlux/GasMassFlux
      XG=WVMFlux/18/(AirMassFlux/MWG0+WVMFlux/18)
    ENDIF

```

C Calculate the number of sorbent particles (for the scavenging case)
 C and the volume of sorbent in each radial shell.

```

IF(Slu.NE.'D') THEN
  R=0
  XRSUM=0

```

```

      ASHSUM=0
      VolSum=0
      DO 107,M=1,NShell(J)
      IF(IVSTOP(J).EQ.0) THEN
        IF(M.LT.NShell(J)) THEN
          NPart(J,M)=NPart(J,M)+(W(2,J)-NPartOld(J))*4*
&          ((R+dR(J,M))**3-R**3)/DropDiam(J)**3
          XRSUM=XRSUM+NPart(J,M)
          NASH(J,M)=NASH(J,M)+(W(3,J)-NASHOLD(J))*4*
&          ((R+dR(J,M))**3-R**3)/DropDiam(J)**3
          ASHSUM=ASHSUM+NASH(J,M)
        ELSE
          NPart(J,M)=W(2,J)-XRSUM
          NASH(J,M)=W(3,J)-ASHSUM
        ENDIF
        R=R+dR(J,M)
      ENDIF
      IF(W(2,J).EQ.0) THEN
        VolPart(J,M)=0
      ELSE
        VolPart(J,M)=.5236*(NPart(J,M)*(1-SP)*WPD(J,M)**3
&          +NASH(J,M)*DASH**3)+VSULFITE(J,M)
      ENDIF
107  VolSum=VolSum+VolPart(J,M)
      ELSE
        VolSum=.5236*(WPD(J,1)**3+(PDO**3-WPD(J,1)**3)*ALPHA)
      ENDIF

```

C Calculate the solid mass in the drop (SMass).

```

      IF(ISTOP(J).EQ.0) THEN
        DUM=0
        IF(IVSTOP(J).EQ.0.AND.Slu.NE.'S') THEN
          DUM=((PDO**3-WPD(J,1)**3)*129/74+WPD(J,1)**3)*W(2,J)
        ELSE
          DO 5,M=1,NSHELL(J)
            IF(WPD(J,M).LT.0) WPD(J,M)=0
5          DUM=DUM+((PDO**3-WPD(J,M)**3)*129/74+WPD(J,M)**3)*NPart(J,M)
          ENDIF
          SMass=3.14159/6*SD*(1-SP)*DUM+DsSolids(J)+W(3,J)*3.14159*
&          DASH**3/6*SD
        ENDIF

```

C Calculate an average sorbent particle diameter for the scavenging case
 C except when W has just been set equal to VAR.

```

      IF(IT.NE.1.AND.W(2,J).GT.NPartOld(J)) THEN
        WPD(J,1)=((NPartOld(J)*WPD(J,1)**3+(W(2,J)-NPartOld(J))*PDD**3)
&          /W(2,J))**.33333333
        DO 105,M=2,NSHELL(J)
105      WPD(J,M)=WPD(J,1)
      ENDIF

```

C Calculate drop diameter, drop density.

```

IF(DropDiam(J).NE.Dmin(J)) THEN
  DropDiam(J)=(1.90986*(W(5,J)*CDO(J)/1E6+VolSum)**.33333333
  IF(VolSum.EQ.0) THEN
    Dmin(J)=0
  ELSE
    Dmin(J)=(1.90986/PACK*VolSum)**.33333333
  ENDIF
  IF(DropDiam(J).LT.Dmin(J).AND.Slu.NE.'D') THEN
    DropDiam(J)=Dmin(J)
    Mevap(J)=0
    ISTOP(J)=1
    R=0
    DO 201,M=1,NShell(J)
      dR(J,M)=(R**3+.75/PACK*VolPart(J,M)/3.14159)**.33333333-R
      R=R+dR(J,M)
      DropDiam(J)=2*R
      Dmin(J)=DropDiam(J)
    ENDIF
  ENDIF

  D2=DropDiam(J)**2
  D3=DropDiam(J)*D2
  IF(ISTOP(J).EQ.0) DropDens=1.90986/D3*(W(5,J)*CDO(J)+SMass)

C Calculate size of differential radial shells.

  IF(Slu.NE.'D'.AND.SO2MFO.NE.0.AND.CaS.NE.0
    & .AND.IT.EQ.1.AND.DropDiam(J).NE.Dmin(J)) CALL DELR(J)

C Calculate the volume of sorbent and product in each radial shell.

  IF(Slu.NE.'D') THEN
    R=0
    DO 108,M=1,NShell(J)
      SolFrac(J,M)=VolPart(J,M)/4.1888888/((R+dR(J,M))**3-R**3)
      R=R+dR(J,M)
    ENDIF
  108

C Determine whether the flux of water due to evaporation should be
C included in SO2 and Ca flux calculations.

  IF(Slu.NE.'D') THEN
    PNSum=0
    R=DropDiam(J)/2
    IF(W(2,J).GT.0.OR.W(3,J).GT.0) THEN
      Dave=(W(2,J)*PDD+W(3,J)*DASH)/(W(2,J)+W(3,J))
    ELSE
      Dave=PDD
    ENDIF
    DO 133,M=NShell(J),1,-1
      IF(SolFrac(J,M).LT..7) GO TO 134
      PNSum=PNSum+NPart(J,M)+NASH(J,M)
      R=R-dR(J,M)
    133
    134 FluxN=6*((DropDiam(J)/2)**3-R**3)/Dave

```

```

      IFlux(J)=0
      IF(PNsum.GT.FluxN) IFlux(J)=1
    ENDIF

```

C Calculate radius of water core.

```

      IF(DropDiam(J).EQ.Dmin(J).AND.ISTOP(J).EQ.0) THEN
        R=0
        WMass=0
        WMold=0
        DO 120,M=1,NSHELL(J)
          WMass=WMass+4.1888*((R+dR(J,M))**3-R**3)*(1-SolFrac(J,M))
          & *1E6
          IF(WMass.LT.W(5,J)*CDO(J)) THEN
            R=R+dR(J,M)
            WMold=WMass
          ELSE
            RWCore(J)=(R**3+((R+dR(J,M))**3-R**3)*((W(5,J)*CDO(J)-WMold)
            & /(WMass-WMold))**.3333333333
            GO TO 125
          ENDIF
        120 CONTINUE
      ENDIF
      IF(ISTOP(J).EQ.0) THEN
        RWCore(J)=DropDiam(J)/2
      ELSE
        RWCore(J)=0
      ENDIF

```

C If water core has receded past a radial shell, store sorbent particle C radius.

```

125 IF(ISTOP(J).EQ.0) THEN
      R=DropDiam(J)
      DO 130,M=NSHELL(J),1,-1
        IF(RdryO(J,M).EQ.0.AND.R.GT.RWCore(J)) RdryO(J,M)=WPD(J,M)/2
130 R=R+dR(J,M)
      ENDIF

```

C Calculate the film temperature (Tf), water mole fraction at the drop C surface (XO), mass fraction in the film (YF) and in the bulk gas C phase (YG), the Gas Mass Rate and Molecular Weights.

```

      IF(ISTOP(J).EQ.1) THEN
        XO=XG
        YF=YG
      ELSEIF(IDRY.EQ.0) THEN
        CASO3=42358/Td-102.56
        DsMol=(DsSolids(J)+CASO3*W(5,J)*CDO(J)/1E6)/W(5,J)/CDO(J)/.111
        ActW=.9899-8.678E-3*DsMol-3.676E-2*DsMol**2+4.624E-3*DsMol**3
        & -1.667E-4*DsMol**4
        IF(Slu.EQ.'D') ActW=1
        XO=ActW*EXP(18.3036-3816.44/(Td-46.13))/P/760
        YF=XO*18/((1-XO)*MWGO+XO*18)

```

```

ELSE
  XO=1
  YF=1
  IDRY=1
ENDIF
IF(XO.GE.1.OR.YF.GE.1) THEN
  XO=1
  YF=1
  IDRY=1
ELSEIF(XO.LE.0.OR.YF.LE.0) THEN
  XO=0
  YF=0
ENDIF
YF=(YF+YG)/2
XF=(XG+XO)/2
MWF=18*XF+MWGO*(1-XF)
MWG=18*XG+MWGO*(1-XG)
DenF=Cf*MWF

IF(XG.LT.0.OR.XG.GT.1.OR.XO.LT.0.OR.XO.GT.1) THEN
  print *, 'xo=', xo, ' xg= ', xg, ' w(6,j)= ', w(6,j)
  RETURN
ENDIF

```

C Calculate drop independent variables.

```
IF(J.EQ.IMIN) THEN
```

C Calculate the SO2 Mass Flux and the SO2 mole fraction in the bulk
C gas phase (YS8).

```

IF(SO2MFO.NE.0) THEN
  SO2MFlux=SO2MFO
  DO 200,L=1,NW
    DUM=0
    IF(IVSTOP(L).EQ.0.AND.Slu.NE.'S') THEN
      DUM=W(2,L)*(PDD**3-WPD(L,1)**3)
    ELSE
      DO 205,M=1,NSHELL(L)
        IF(Slu.NE.'D') THEN
          DUM=DUM+NPart(L,M)*(PDD**3-WPD(L,M)**3)
        ELSE
          IF(L.EQ.1) THEN
            DUM=DUM+(PDO**3-WPD(L,M)**3)
          ELSE
            DUM=DUM+(PDR0**3-WPD(L,M)**3)
          ENDIF
        ENDIF
      ENDIF
    CONTINUE
  ENDIF
  SO2MFlux=SO2MFlux-DropNFlux(L)/(1.90986/(1-SP))/VolMol
  &      *(1-CaUt)*DUM
  YS8=SO2MFlux/(AirMassFlux/MWGO+WVMFlux/18+SO2MFlux)
  IF(YS8.LE.0) THEN

```

```

      ICease=1
      RETURN
    ENDIF
  ENDIF

```

```

C Calculate viscosities (Mu or Vis), heat capacities (Cp or HtCap),
C molecular weights (MW), thermal conductivities (Cond), heat of
C vaporization (HTVAP), and densities (Den) for air (A), gas (G),
C water (W), and film (F).
C Calculate bulk diffusivity of SO2 and coefficient of external mass
C transfer.
C Calculate calcium hydroxide diffusivity in water (Dlime), equilibrium
C concentration of lime in water (CLimeEq), and Henry's Constant.
C Calculate Henry's Constant.

```

```

      IF(ISTOP(NW).EQ.0.AND.ABS(Tg-TGold).GT.0.5) THEN
        MuAir=2.484E-4*Tg**.7319
        MuW=2.109E-5*Tg**1.0776
        VisG=(1-YG)*MuAir+YG*MuW
        CpA=(28.09+.1965E-2*Tg+.4799E-5*Tg**2-1.965E-9*Tg**3)
        CpW=(33.46+.688E-2*Tg+.7604E-5*Tg**2-3.593E-9*Tg**3)
        TC=Tg-273
        CpCO2=(36.11+4.233E-2*TC-2.887E-5*TC**2+7.464E-9*TC**3)
        HtCapG=((1-XG)*(1-CO2)*CpA+XG*CpW+CO2*(1-XG)*CpCO2)/MWG
        TGold=Tg
      ENDIF
      DenG=DenG*MWG
    ENDIF

```

```

      IF(ISTOP(J).EQ.0) THEN
        MuAir=2.484E-4*Tf**.7319
        MuW=2.109E-5*Tf**1.0776
        VisF=(1-YF)*MuAir+YF*MuW
        CondA=2.032E-4*Tf**.8522
        CondW=2.593E-5*Tf**1.154
        CondF=(1-YF)*CondA+YF*CondW
        DSO2=3.851E-10*Tf**1.824
        Sc=VisF/DenF/DSO2
        IF(IVSTOP(J).EQ.0) THEN
          DeltaV=W(4,J)-GV
          Re=DropDiam(J)*DeltaV/(VisF/DenF)
          Sh=2+.6*SQRT(Re)*Sc**.33333333
        ELSE
          Sh=2
        ENDIF
        CMTSO2=Sh*DSO2/DropDiam(J)*Cf
      ENDIF

```

```

      IF(ABS(Td-TDold).GT.0.5.OR.Slu.EQ.'A'.AND.DeltaV.GT..4*DelV0.
&      AND.DeltaV.LT..45*DelV0) THEN
        HTVAP=(2.897E5*Td**(-.3309)+5.703E4-43.68*Td)/2
        HtCapW=3.251*Td**.044
        CpA=(28.09+.1965E-2*Td+.4799E-5*Td**2-1.965E-9*Td**3)
        CpW=(33.46+.688E-2*Td+.7604E-5*Td**2-3.593E-9*Td**3)

```

```

D1ime=3.954E-9*Td*EXP(-2046/Td)
CLimeEq=16550/Td-35.62
HE=EXP(2.4717-2851.1/Td)
KDISSOC=EXP(22.426-1775/Td-.046*Td)
DH2SO3=Td*EXP(-19.895-1800/Td)
DHSO3=1.7856E-13*Td/(1/(4.86*Td-1100)+1/(1.46*Td-390))
TDo1d=Td
ENDIF
TC=Td-273
CpCO2=(36.11+4.233E-2*TC-2.887E-5*TC**2+7.464E-9*TC**3)
HtCapF=((1-XF)*(1-CO2)*CpA+XF*CpW+CO2*(1-XF)*CpCO2)/MWF

```

C Calculate the difference between drop and gas velocities (DeltaV),
C Reynolds (Re), Schmidt (Sc), Prandtl (Pr), Sherwood (Sh), and
C Nusselt (Nu) numbers and the water diffusivity in the film (Dv).

```

Dv=4.3E-11*Tf**2.334/P
IF (IVSTOP(J).EQ.1.OR.W(4,J)-GV.LE..01) THEN
  W(4,J)=GV
  Re=0
  ReG=0
  Sh=2
  Nu=2
  IVSTOP(J)=1
ELSE
  DeltaV=W(4,J)-GV
  ReG=DropDiam(J)*DeltaV*DenG/VisG
  Sc=VisF/DenF/Dv
  Re=DropDiam(J)*DeltaV/(VisF/DenF)
  Pr=HtCapF*VisF/CondF
  Sh=2+.6*SQRT(Re)*Sc**.33333333
  Nu=2+.6*SQRT(Re)*Pr**.33333333
ENDIF

```

C Calculate water Heat Transfer Coefficient in the film and heat flow to
C the drop (Q).

```

HTC=Nu*CondF/DropDiam(J)
Q=3.14159*D2*(Tg-Td)*HTC

```

C Calculate the drop evaporation rate (ERate) and the heat flow
C to the drop (Q).

```

IF (ISTOP(J).EQ.0.AND.IDRY.EQ.0) THEN
  CMTW=Sh*Dv/DropDiam(J)
  IF (Mevap(J).NE.0) THEN
    ER=-Cf*CMTW*ALOG((1-X0)/(1-XG))
  ELSE
    Cd=P/8.206E-5/Td
    Deff=.25*Dv
    A=Deff*Cd/DropDiam(J)*2*RWCore(J)/(RWCore(J)-DropDiam(J)/2)
    ER=-Cf*(XG-X0)/(1/CMTW-1/A)
  C print *, 'a=', a, ' cmtw=', cmtw, ' er=', er

```



```

C      print *, 'Td=', w(6,1)*t0, w(5,1), 'MEVAP=', MEVAP(j)
C      print *, 'dmin=', dmin, 'Dm', dropdiam(j)
      ENDIF
      ERate=3.14159*D2*ER
    ELSE
      ERate=0
      ER=0
    ENDIF

    IF(ERate.NE.0.AND.IDRY.EQ.0) THEN
      EP=9./3.14159*ERate*18*HtCapF/CondF/UropDiam(j)
      IF(EP.LT.88) THEN
        Q=Q*EP/(EXP(EP)-1)
      ELSE
        Q=0
      ENDIF
    ENDIF

  ENDIF

RETURN
END

```

```

SUBROUTINE DELR(J)
C Calculate size of radial differential shells.

REAL DropDiam(15),dR(15,50)
REAL VolPart(15,50)
INTEGER NSHELL(15),Mevap(15),ISTOP(15)

COMMON/DROP/DropDiam
COMMON/DR/dR
COMMON/NS/NSHELL
COMMON/MEVAP/Mevap
COMMON/VL/VolPart
COMMON/I/ISTOP
COMMON/PACK/PACK
common/dis/dis

IF(Mevap(J).EQ.0) RETURN

C In each shell, calculate the volume of solids (VolPart), the minimum
C delta radius (delR) which is based on a close packing of 75% solid
C spheres.

R=DropDiam(J)/2
DO 10,M=NSHELL(J),1,-1

C If the shell has stopped evaporating set dR to the close packing value.

IF(M.GT.Mevap(J)) THEN
  IF(R**3.GT..75/PACK*VolPart(J,M)/3.14159) THEN
    dR(J,M)=R-(R**3-.75/PACK*VolPart(J,M)/3.14159)**.3333333
  ELSE
    Mevap(J)=0
    ISTOP(J)=1
    R=0
    DO 201,L=1,NShell(J)
      dR(J,L)=(R**3+.75/PACK*VolPart(J,L)/3.14159)**.3333333-R
    201 R=R+dR(J,L)
    DropDiam(J)=2*R
    RETURN
  ENDIF

C If the shell is the evaporating shell calculate dR and the close
C packing dR and, if dR is less than delRmin set equal to delRmin.

ELSEIF(M.EQ.Mevap(J)) THEN

  dR(J,M)=R-(M-1)*dR(J,1)
  IF(R**3.GT..75/PACK*VolPart(J,M)/3.14159) THEN
    delRmin=R-(R**3-.75/PACK*VolPart(J,M)/3.14159)**.3333333
  ELSE
    Mevap(J)=0

```

```

      R=0
      DO 200,L=1,NShell(J)
200    dR(J,L)=(R**3+.75/PACK*VolPart(J,L)/3.14159)**.33333333-R
      R=R+dR(J,L)
      DropDiam(J)=2*R
      RETURN
    ENDIF

    IF(dR(J,M).LE.delRmin) THEN
      dR(J,M)=delRmin
      Mevap(J)=Mevap(J)-1
    ENDIF

    ELSEIF(M.LT.Mevap(J)) THEN
      RETURN
    ENDIF

10    R=R-dR(J,M)

    RETURN
  END

```

SUBROUTINE FLX(J,ER,SMF)

C This subroutine calculates concentration from the second-order
C differential equation of C with respect to R using a
C 4th order Runge-Kutta method.

```

IMPLICIT REAL (K)
REAL dR(15,50),KDISSOC,RWCore(15),dRSO2(15)
REAL ShellFlux(15,50),CDO(15)
REAL DropDiam(15),W(7,15),WPD(15,50),NPart(15,50)
REAL MolWt,SolFrac(15,50),RFRONT(15),CO(15)
REAL *8 R,xdR,Rold1(15),RO,Rmin,Rmax,Z,XS8,YS8CALC
REAL *8 YS8OLD(15),dCdR
REAL CP(0:55)
INTEGER NSHELL(15),NStart(15),Mevap(15),IFlux(15)

```

```

COMMON/DUM/W,WPD
COMMON/DR/dR
COMMON/SO2/DSO2,CMTSO2,HE,KDISSOC,DH2SO3,DHSO3,YS8
COMMON/NS/NSHELL
COMMON/NT/NStart
COMMON/RW/RWCore
COMMON/DROP/DropDiam
COMMON/MEVAP/Mevap
COMMON/NPDR/NPart
COMMON/VOL/VolMol,CaUt
COMMON/MOL/MolWt
COMMON/CO/CO
COMMON/SS/dRSO2
COMMON/ROLD/Rold1
COMMON/ICE/ICEASE
COMMON/SHEL/ShellFlux
COMMON/MOLD/Mold
COMMON/LIME/Dlime,ClimeEq
COMMON/IF/IFlux
COMMON/SOL/SolFrac
COMMON/P/CDO,SMFO
COMMON/PACK/PACK
COMMON/RF/RFRONT
common/dis/dis
common/cas/cas
common/emt/emratio
ipz=5

```

```

DO 113,M=1,NShell(J)
113 IF(WPD(J,1).GT.0) GO TO 114
RETURN

```

C SO2 concentration profiles are calculated using a separate set of
C radial shells. The term droplet radial shell will refer to the radial
C shells used throughout the rest of the program and the term L shells
C will refer to the radial shells used in this subroutine to calculate
C the SO2 concentration profile.

```

114 IF(CO(J).EQ.0) THEN
      IDIV2=0
    ELSE
      IDIV2=1
    ENDIF

    ISC=1
    XS8=YS8
    Rmin=0
    Rmax=DropDiam(J)/2
    RO=Rmax-dRSO2(J)
    IF(dRSO2(J).EQ.0.AND.WPD(J,NShell(J)).EQ.0) RO=DropDiam(J)*.4998
    Mold=0
    IF(RO.LT.0.OR.CO(J).GT.0.AND.CO(J).LE.1E-6) CO(J)=2E-6
    dCdREMT0=CMTSO2*YS8/Dlime
    dCdRO=0
    IF(IFlux(J).EQ.1) dCdRO=ER/Dlime/55334
    Cmin=0
    CSMAX=SQRT(YS8*KDISSOC/HE)
    Cmax=CSMAX
    IF(CO(J).NE.0) THEN
      CP(0)=CO(J)
    ELSE
      CP(0)=0
    ENDIF
    IDC=0
    IDiverge=0

10   IDiverge=IDiverge+1
    IF(RO.LT.0) RO=0
    IF(IDiverge.EQ.45) THEN

      IF(ER.GT.0) THEN
        DO 650,L=1,NSHELL(J)
650   ShellFlux(J,L)=0
        RETURN
      ENDIF

      PRINT *, '*****'
      PRINT *, '***SECANT METHOD HAS DIVERGED. PROGRAM TERMINATED***'
      PRINT *, '*****'
      print*, ' j=',j, ' r0=',r0, ' rmin=',rmin, ' rmax=',rmax
      print *, 'ys8=',ys8, 'ys8c=',ys8calc, ' idiverge=',idiverge
      &      ' idiv2=',idiv2
      print *, 'rwcore=',rwcore(J), ' diam/2=',dropdiam(J)/2
      print *, 'L, sorbent diameters= , dR= , '
      &      ' Npart= , SHLFLUX='
      do 799,l=NSTART(J),nshell(J)
799   print *,l,wpd(j,l),dr(j,l),NPart(j,l),Shellflux(j,l)
      do 800,l=0,11
800   print *, 'cp(',l,')=',cp(l)
      ICEASE=1
      RETURN
    ENDIF

```

C Find initial radial shell position. Calculate VRR, the volume of the
 C droplet radial shell/Pi.
 C RR is the radius of the outer edge of the droplet radial shell.
 C R is the inner edge of L shell.

```

    IF(CO(J).NE.0.AND.DropDiam(J)/2.EQ.RWCore(J)) THEN
      M=1
      NStart(J)=1
      R=0
      CP(0)=CO(J)
      VRR=dR(J,1)**3
      RR=dR(J,1)
    ELSE
      RR=0
      CP(0)=0
      DO 15,M=1,NShell(J)
        RR=RR+dR(J,M)
  C Do not remove the following if statement.
        if(dis.le.-9999)print*,'m=',m,' rr=',
&          rr,' r0=',r0
        IF(RR.GE..9999999*R0) THEN
          NStart(J)=M
          GO TO 16
        ENDIF
  15  CONTINUE
      ENDIF
      IF(CO(J).EQ.0) THEN
        R0=(Rmin+Rmax)/2
        GO TO 10
      ENDIF

  C Calculate calcium profile.*****

  16  IF(CO(J).EQ.0) THEN
      CALL CA(J,R,R0,dCdR,dCdREMT0,dCdR0,VRR,ER,IRWARN)
      IF(IRWARN.EQ.1) THEN
        IRWARN=0
        R0=.999*R0
        GO TO 10
      ENDIF
      IF(ICEASE.EQ.1) RETURN
      dCdR=-Dlime/DHSO3*dCdR
      R=R0
    ELSE
      dCdR=0
    ENDIF

    IF(ShellFlux(J,NStart(J)).LT..99*ShellFlux(J,NStart(J)-1).AND.
&      NStart(J).NE.1) THEN
      Rmax=R0
      R0=(.5+.17*ISC+IDiverge/400.)*(Rmax-Rmin)+Rmin
      ISC=-ISC
      GO TO 10

```

ENDIF

```
IF(ABS(R0-DropDiam(J)/2).LT..00005*DropDiam(J)/2) THEN
  R0=RWCore(J)
  xs=0
  GO TO 30
ENDIF
```

C Calculate sulfur profile.*****

```
IN=15./(NShell(J)-NStart(J)+1)+.999999999
IF(IN.LT.2) IN=2
LL=IN*(NShell(J)-NStart(J)+1)
ILERT=0
Mold=0
DO 20,L=1,LL

  ICOUNT=ICOUNT+1
  IF(L/FLOAT(IN)-INT(L/IN).LT..01) ICOUNT=0
  IF(ICOUNT.EQ.1.AND.L.NE.1) THEN
    ShellFlux(J,M)=4*R**2*dCdR*(2*DH2SO3*CP(L-1)/KDISSOC+DHSO3)
    IF(IFlux(J).EQ.1.AND.SolFrac(J,M).GT..95*PACK) ShellFlux(J,M)=
    & ShellFlux(J,M)+CP(L-1)*ER/55334*4*R**2
    M=M+1
    IF(M.NE.NStart(J)) THEN
      xdR=dR(J,M)/IN
    ELSE
      xdR=(RR-R0)/IN
    ENDIF
    RR=RR+dR(J,M)
    VRR=RR**3-(RR-dR(J,M))**3
  ELSEIF(L.EQ.1) THEN
    xdR=(RR-R0)/IN
  ENDIF
```

C Perform Runge-Kutta.

```
18  K11=xdR*dCdR
    K12=xdR*DIFF(CP(L-1),dCdR,R,xdR,J,M,VRR,ILERT,ER)
    K21=xdR*(dCdR+K12/2)
    K22=xdR*DIFF(CP(L-1)+K11/2,dCdR+K12/2,R+xdR/2,xdR,J,M,VRR,ILERT
    & ,ER)
    K31=xdR*(dCdR+K22/2)
    K32=xdR*DIFF(CP(L-1)+K21/2,dCdR+K22/2,R+xdR/2,xdR,J,M,VRR,ILERT
    & ,ER)
    K41=xdR*(dCdR+K32)
    K42=xdR*DIFF(CP(L-1)+K31,dCdR+K32,R+xdR,xdR,J,M,VRR,ILERT,ER)
```

C For the case when a radial shell has not been encountered (INSEC=0).
C For the case when a radial shell has been encountered (INSEC=1),
C up to the outer radius of the droplet radial shell.
C For the case after a radial shell has been encountered (INSEC=2),
C up to the outer radius of the L shell.

```

CP(L)=CP(L-1)+(K11+2*K21+2*K31+K41)/6
dCdR=dCdR+(K12+2*K22+2*K32+K42)/6

```

C If ShellFlux wasn't calculated above, (for CO.NE.0) calculate here.

```

IF(CO(J).NE.0.OR.L.EQ.LL) THEN
  ShellFlux(J,M)=4*(R+xdR)**2*dCdR*(2*DH2SO3*CP(L)/KDISSOC+DHSO3)
  IF(IFlux(J).EQ.1.AND.SolFrac(J,M).GT..95*PACK) ShellFlux(J,M)=
&      ShellFlux(J,M)+CP(L-1)*ER/55334*4*(R+xdR)**2
ENDIF

```

C If CP is decreasing or becoming to big, assign new Rmin value.

```

23  IF(L.EQ.LL.AND.CP(L).LT.CP(L-1).AND.CO(J).EQ.0.AND.WPD(J,M)
&      .EQ.0.) THEN
    Rmax=R0
    R0=.25*(Rmax-Rmin)+Rmin
    GO TO 10
  ELSEIF(CP(L).LT.CP(L-1).AND.CO(J).EQ.0) THEN
    Rmin=R0
    R0=.3*(Rmax-Rmin)+Rmin
    GO TO 10
  ELSEIF(CP(L).GT.2*CSMAX.AND.CO(J).EQ.0) THEN
    Rmin=R0
    R0=.7*(Rmax-Rmin)+Rmin
    GO TO 10
  ELSEIF(CO(J).NE.0.AND.CO(J).LT.1E-10) THEN
    GO TO 307
  ELSEIF(CP(L).LT..85*CP(L-1).AND.CO(J).NE.0) THEN
    Cmax=CO(J)
    CO(J)=.67*(Cmax-Cmin)+Cmin
    GO TO 10
  ELSEIF(CP(L).GT.1.2*CSMAX.AND.CO(J).NE.0) THEN
    Cmax=CO(J)
    CO(J)=.25*(Cmax-Cmin)+Cmin
    GO TO 10
  ENDIF

```

20 R=R+xdR

C Check to see if the calculated ambient concentration equals the
C actual ambient concentration of SO2. If not, correct the
C guessed concentration using the secant method.

```

IF(ILERT.EQ.0) THEN
  XS=HE*CP(LL)**2/KDISSOC
  AA=dCdR*(2*DH2SO3*CP(LL)/KDISSOC+DHSO3)+(CP(LL)+CP(LL)**2/
&      KDISSOC)*ER/55334
  ELSE
    XS=CP(LL)
    AA=dCdR
  ENDIF

```

YS8CALC=(XS*(CMTS02-ER-AA)+AA)/CMTS02


```

      IF(DABS(XS8-YS8CALC).LT..001*XS8.OR.
      & Rmax-Rmin.LT.1D-5*Rmin.AND.IDiverge.GT.20.OR.
      & IDiverge.GT.25.AND.IDIV2.EQ.2.AND.R0.LT.2D-8) GO TO 30

```

C Calculate new CO for the case where SO2 diffuses to the droplet center.

```

307  IF(CO(J).NE.0) THEN

```

C Switch to the case where SO2 drops to zero at some point not at the C center.

```

      IF(CO(J).LT.1E-10) THEN
        R0=.7*(Rmax-Rmin)+Rmin
        Rold1(J)=.001*DropDiam(J)
        YS8OLD(J)=YS8CALC
        CO(J)=0
        CP(0)=0
        IDC=0
        IDIV2=IDIV2+1
        IDIVERGE=0
        GO TO 10

```

```

      ENDIF

```

C Reassign new Cmin or Cmax value.

```

      IF(CO(J).LT.Cmax.AND.YS8CALC.GT.YS8) THEN
        Cmax=CO(J)
      ELSEIF(CO(J).GT.Cmin.AND.YS8CALC.LT.YS8) THEN
        Cmin=CO(J)
      ENDIF

```

```

      IF(YS8CALC.GT.1) THEN
        CO(J)=CO(J)/2
        Cold1=0
        YS8OLD(J)=0

```

```

      ELSE

```

```

        Z2=CO(J)

```

```

        IF(CO(J).EQ.Cold1) THEN

```

```

          CO(J)=CO(J)*.99

```

```

        ELSE

```

```

          CO(J)=CO(J)-(YS8-YS8CALC)/(YS8OLD(J)-YS8CALC)*
          (CO(J)-Cold1)

```

```

      &

```

```

        IF(CO(J).EQ.0) CO(J)=1D-5

```

```

        IF(CO(J).GT.Cmax) THEN

```

```

          CO(J)=.7*(Cmax-Cmin)+Cmin

```

```

        ELSEIF(CO(J).LT.Cmin) THEN

```

```

          CO(J)=.3*(Cmax-Cmin)+Cmin

```

```

        ENDIF

```

```

        Cold1=Z2

```

```

        ENDIF

```

```

      ENDIF

```

```

      CP(0)=CO(J)

```

C For the case where sulfur drops to zero away from the droplet center.

ELSE

C Reassign new Rmin or Rmax value.

```
IF(R0.LT.Rmax.AND.YS8CALC.LT.YS8) THEN
  Rmax=R0
ELSEIF(R0.GT.Rmin.AND.YS8CALC.GT.YS8) THEN
  Rmin=R0
ENDIF
```

C Switch to sulfur diffusion to the center if necessary.

```
IF(Rmax-Rmin.LT..002*DropDiam(J)/2.AND.R0.LT.DropDiam(J)/50
& .AND.IDiverge.GT.20.AND.Rold1(J).LT.DropDiam(J)/50.AND.IDIV2
& .LT.2) THEN
  CO(J)=CP(1)*2
  CoId1=CP(1)
  IDIVERGE=0
  R0=0
  IDIV2=IDIV2+1
  IDC=0
  GO TO 10
ENDIF
```

C Calculate new R0.

```
IF(IDiverge.GE.10.and.IDiverge.LT.15.OR.IDiverge.GE.30.AND.
& IDiverge.LT.35) THEN
  IF(IIC.EQ.0) THEN
    R0=(.33+IDiverge/400.)*(Rmax-Rmin)+Rmin
    IIC=1
  ELSE
    R0=(.67+IDiverge/400.)*(Rmax-Rmin)+Rmin
    IIC=0
  ENDIF
ELSE
  Z=R0
  R0=R0-(XS8-YS8CALC)/(YS8OLD(J)-YS8CALC)*(R0-Rold1(J))
  IF(IDIVERGE.EQ.1) THEN
    R0=DropDiam(J)/2-1.005*(DropDiam(J)/2-Z)
  ENDIF
  IF(R0.GT.DropDiam(J)/2) THEN
    IF(Rold1(J).EQ.0) THEN
      R0=(Rmin+Rmax)/2
    ELSE
      R0=.8*(Rmax-Rmin)+Rmin
    ENDIF
  ELSEIF(R0.GT.Rmax) THEN
    R0=.7*(Rmax-Rmin)+Rmin
  ELSEIF(R0.LT.Rmin) THEN
    R0=.3*(Rmax-Rmin)+Rmin
  ENDIF
  IF(R0.EQ.Z) R0=.67*(R0-Rmin)+Rmin
  IF(R0.EQ.Z) R0=.33*(Rmax-R0)+R0
```

```

        Ro1d1(J)=Z
      ENDIF
    ENDIF
    YS8OLD(J)=YS8CALC
    GO TO 1\

30    dRSO2(J)=RWCore(J)-RO
    SHOLD=SHELLFLUX(J,NSHELL(J))
    IF(Rmax-Rmin.LT.1D-5*Rmin.AND.YS8CALC.LT..98*YS8) THEN
        IF(ICease.EQ.0) ICease=10
        ICease=ICease-1
    ENDIF
    ShellFlux(J,NShell(J))=SHOLD
    RFRONT(J)=RO
    emratio=(cmtso2*(ys8-xs)+xs*er)/cmtso2/ys8

    if(dis.ge.9999.and.j.ne.0.and.dis.lt.2.411.or.ipz.eq.1) then
        su1fnc=6*volmol*dropdiam(J)**2/wpd(1,1)**3/w(2,j)*(cmtso2*
&      (ys8-xs)+xs*er)*100*cas*SMF/SMFO
        axemt=6*volmol*dropdiam(J)**2/wpd(1,1)**3/w(2,j)*cmtso2*
&      ys8*100*cas*SMF/SMFO
        RD=RO/DROPDIAM(j)*2
        emratio=(cmtso2*(ys8-xs)+xs*er)/cmtso2/ys8
        if(dis.gt.99) then
            r=dropdiam(J)/2
            do 7,l=11,1
7          r=r-xdr
            endif
            endif
1          FORMAT(1X,3(A,E9.3),2(A,I2),1(A,E9.3),A,F5.0,A,I2)
          RETURN
        END

```

FUNCTION DIFF(C,dCdR,R,dR,J,M,VRR,ILERT,ER)

C Second order differential equation governing diffusion of SO2
C the droplet or agglomerate.

REAL W(7,15),WPD(15,50),NPART(15,50),RWCore(15),KDISSOC
REAL Rdry0(15,50),SolFrac(15,50)
REAL *8 R,dR,dCdR
INTEGER Mevap(15),IFlux(15)

COMMON/DUM/W,WPD
COMMON/SA/RoughK
COMMON/SO2/DSO2,CMTSO2,HE,KDISSOC,DH2SO3,DHSO3,YS8
COMMON/AG/DissRate,RateK,Dprod
COMMON/LIME/Dlime,ClimeEq
COMMON/NPDR/NPart
COMMON/E/SD,PD0,SP,PDD
COMMON/MEVAP/Mevap
COMMON/RW/RWCore
COMMON/RD/Rdry0
COMMON/A/ALPHA
COMMON/SOL/SolFrac
COMMON/MOLD/Mold
COMMON/IF/IFlux
COMMON/PACK/PACK
common/dis/dis

IF(M.NE.Mold) Rough=1+EXP(RoughK*((WPD(J,M)/PD0)**3-.8))
IF(ILERT.EQ.0) THEN

C Liquid phase mass transfer.

A=2*DH2SO3/KDISSOC*C+DHSO3
B=2*DH2SO3/KDISSOC*dCdR
IF(R.NE.0) B=B+2*A/R
IF(IFlux(J).EQ.1.AND.SolFrac(J,M).GT..95*PACK) B=B+(1+2*C/
& KDISSOC)*ER/55334

IF(IFlux(J).EQ.1.AND.SolFrac(J,M).GT..95*PACK) THEN
EVTERM=(C+C**2/KDISSOC)*ER*2/R/55334
ELSE
EVTERM=0
ENDIF

IF(WPD(J,M).GT.0) THEN
IF(M.NE.Mold.OR.J.NE.Jold) THEN
U=4*Dlime*ClimeEq
V=4*Dlime/Rough/DissRate/WPD(J,M)**2
EP=NPart(J,M)/VRR/1.33333
DUM2=1/Rough/DissRate/WPD(J,M)**2
ENDIF
dmoldt=CLimeEq/(DUM2+(2/WPD(J,M)-1/(WPD(J,M)/2+
& Del(C,WPD(J,M),U,V,J,M)))/4/Dlime)
DIFF=(dmoldt*EP/(1-SolFrac(J,M))-EVTERM-B*dCdR)/A

```

ELSE
  DIFF=(-EVTERM-B*dCdR)/A
ENDIF

ELSE
  C Gas phase mass transfer through dried agglomerate.

  Deff=DSO2*(1-SolFrac(J,M))
  IF(Rdry0(J,M).EQ.0) THEN
    Rdry0(J,M)=WPD(J,M)/2
    B=0
  ELSE
    Rratio=1/(ALPHA*(2*Rdry0(J,M)/WPD(J,M))**3+1-ALPHA)**.33333333
    B=12.5664*NPart(J,M)/((R+dR)**3-R**3)*
    & (WPD(J,M)/2)**2/Deff/(1/Ratek/Rough+WPD(J,M)/2/
    & Dprod*(1-Rratio))
  ENDIF
  DIFF=B*C-2/R*dCdR

ENDIF

Mold=M
Jold=J
RETURN
END

FUNCTION DEL(C,PD,U,V,J,M)

REAL KDISSOC,SolFrac(15,50)
COMMON/SOL/SolFrac
COMMON/SO2/DSO2,CMTSO2,HE,KDISSOC,DH2SO3,DHSO3,YS8

Delta=(1/SolFrac(J,M)**.333333-1)
IF(Delta.GT.1) Delta=1
Delta=Delta*PD/2
IF(C.GT.0) THEN
  T=DHSO3*C+2*DHSO3*C**2/KDISSOC
  Del=(U+T)/(2*T/PD+T*V+U/(PD/2+Delta))-PD/2
ELSE
  Del=Delta
ENDIF

RETURN
END

```

SUBROUTINE CA(J,R,RO,dCdR,dCdREMT0,dCdRO,VRR,ER,IRWARN)

C This subroutine calculates concentration from the second-order
C differential equation of C with respect to R using a
C 4th order Runge-Kutta method.

IMPLICIT REAL (K)
REAL dR(15,50),KDISSOC,NPart(15,50)
REAL ShellFlux(15,50),SolFrac(15,50),DropDiam(15)
REAL *8 R,xdR,RO,Z,Cld
REAL *8 dCdR,Cmax,Cmin,CCa(200)
REAL *8 CCa0(15),ColD(15),dCdRgoal,dCdROld,C,CCa00ld
INTEGER NStart(15),Mevap(15),NShell(15),MStart(15),IFlux(15)

COMMON/DR/dR
COMMON/SO2/DSO2,CMTSO2,HE,KDISSOC,DH2SO3,DHSO3,YS8
COMMON/NT/NStart
COMMON/DROP/DropDiam
COMMON/MEVAP/Mevap
COMMON/ICE/ICEASE
COMMON/SHEL/ShellFlux
COMMON/LIME/Dlime,CLimeEq
COMMON/CCA0/CCa0
COMMON/NS/NSHELL
COMMON/MOLD/Mold
COMMON/CLEDUM/CLEdum
COMMON/NPDR/NPart
COMMON/IF/IFlux
COMMON/SOL/SolFrac
COMMON/PACK/PACK
common/dis/dis
common/pz/ipz

C Calculate calcium profile.*****
C Calculate flux of Ca from each shell (flux/pi).

IMAX=50*NShell(J)
ITotal=0
CLEdum=CLimeEq
IF(CCa0(J).GE.CLimeEq) CCa0(J)=.99*CLimeEq
MStart(J)=MStart(J)-1
IF(MStart(J).LE.0.OR.MStart(J).GT.NStart(J)) MStart(J)=1
Mold=0
MINUS=0
10 ICa=0
Cmin=0
Cmax=CLimeEq
IF(MStart(J).NE.1) CCa0(J)=.99*CLimeEq
CCa0old=0
199 ICa=ICa+1
ITotal=ITotal+1

IF(ICa.EQ.55.OR.ITotal.EQ.IMAX) THEN

```

      IF (RO.EQ.DropDiam(J)/2.AND.Cmax-Cmin.LT..000000001*CMIN) THEN
        IRWARN=1
        RETURN
      ENDIF
      PRINT *, '*****'
      PRINT *, '***Calcium profile diverged. Program terminated***'
      PRINT *, '*****'
      ICEASE=1
      PRINT 4, 'ICa=', ICa, ' ITotal=', ITotal, ' MStart=', MStart(J),
        & ' NStart=', NStart(J), ' IMAX=', IMAX
      FORMAT(1X,A,I2,A,I4,2(A,I2),A,I4)
      RETURN
    ENDIF
    dCdR=0
    C=CCaO(J)
    R=
  )
  IN=15./(NStart(J)-MStart(J)+1)+.99999999
  IF (IN.LT.2) IN=2
  NCa=IN*(NStart(J)-MStart(J)+1)

  DO 100, MM=1, MStart(J)-1
    R=R+dR(J,MM)
100  RR=RR+dR(J,MM)

  DO 101, M=MStart(J)-1
    ICOUNT=0
    DO 200, L=1, NCa
      ICOUNT=ICOUNT+1
      IF (L/FLOAT(IN)-INT(L/IN).LT..01) ICOUNT=0
      IF (ICOUNT.EQ.1) THEN
        IF (M.NE.0) THEN
          IF (IFlux(J).EQ.1.AND.SolFrac(J,M).GT..95*PACK) THEN
            ShellFlux(J,M)=-4*R**2*(dCdR*Dlime-ER*C/55334)
          ELSEIF (L.NE.1) THEN
            ShellFlux(J,M)=-4*R**2*dCdR*Dlime
          ENDIF
        ENDIF
        M=M+1
        IF (M.NE.NStart(J)) THEN
          xdR=dR(J,M)/IN
        ELSE
          xdR=(RO-RR)/IN
        ENDIF
        RR=RR+dR(J,M)
        VRR=RR**3-(RR-dR(J,M))**3
      ENDIF

      K11=xdR*dCdR
      K12=xdR*CaDif(C,dCdR,R,J,M,VRR,ER)
      K21=xdR*(dCdR+K12/2)
      K22=xdR*CaDif(C+K11/2,dCdR+K12/2,R+xdR/2,J,M,VRR)
      K31=xdR*(dCdR+K22/2)

```

```

K32=xdR*CaDif(C+K21/2,dCdR+K22/2,R+xdR/2,J,M,VRR,ER)
K41=xdR*(dCdR+K32)
K42=xdR*CaDif(C+K31,dCdR+K32,R+xdR,J,M,VRR,ER)

Cld=C
C=C+(K11+2*K21+2*K31+K41)/6
CCa(L)=C
IF(C.LT.-2000.OR.C.GT.0.AND.Cld.LE.0.AND.L.NE.1) THEN
  Cmin=CCa0(J)
  CCa0(J)=(.74-ICa/400.)*(Cmax-Cmin)+Cmin
  GO TO 199
ENDIF
IF(C.GT.Cld.AND.dCdR.GT.0) THEN
  Cmax=CCa0(J)
  CCa0(J)=(.74-ICa/400.)*(Cmax-Cmin)+Cmin
  GO TO 199
ENDIF
IF(C.LT.0.AND.L.LT.NCa.AND.R0.EQ.DropDiam(J)/2) THEN
  Cmin=CCa0(J)
  CCa0(J)=(.6-ICa/400.)*(Cmax-Cmin)+Cmin
  GO TO 199
ENDIF
dCdR=dCdR+(K12+2*K22+2*K32+K42)/6
200 R=R+xdR

```

C Calculate new CCa0(J) based on setting C(R0) = 0 when R0 isn't at the C drop surface or setting flux at the drop surface equal to the maximum C rate of external mass transfer.

```

Z=CCa0(J)
IF(ABS(R0-DropDiam(J)/2).GT..0001*DropDiam(J)/2) THEN
  IF(ABS(C).LT.1E-2) GO TO 201
  IF(Cmax-Cmin.LT..0000000000000001*CMIN.AND.Mstart(J).NE.
&      NStart(J)) THEN
    Mstart(J)=Mstart(J)+1
    MINUS=1
    GO TO 10
  ENDIF
  IF(C.GT.CLimeEQ.OR.C.GT.0.AND.CCa0(J).LT.Cmax.AND.C.LT.Cld)
&      THEN
    Cmax=CCa0(J)
  ELSEIF(C.LT.0.AND.CCa0(J).GT.Cmin) THEN
    Cmin=CCa0(J)
  ENDIF

  TINY=1E-15
  CCa0(J)=CCa0(J)-C/(C-COLD(J)+TINY)*(CCa0(J)-CCa0old)
  COLD(J)=C
  ELSEIF(ABS(R0-DropDiam(J)/2).LT..0001*DropDiam(J)/2) THEN
    dCdRgoal=-dCdREMT0+dCdR0*C
    IF(ABS(dCdR-dCdRgoal).LT.ABS(.001*dCdR)) GO TO 201
    IF(Cmax-Cmin.LT..0000000000000001*CMIN.AND.Mstart(J).NE.
&      NStart(J)) THEN

```



```

        MStart(J)=MStart(J)+1
        MINUS=1
        GO TO 10
    ENDIF

    IF(C.GT.CLimeEQ.OR.dCdR.GT.dCdRgoal.AND.CCa0(J).
    & LT.Cmax.and.dCdR.LT.0) THEN
        Cmax=CCa0(J)
    ELSEIF(C.LT.0.AND.CCa0(J).GT.CCa0old.OR.dCdR.LT.dCdRgoal.
    & AND.CCa0(J).GT.Cmin) THEN
        Cmin=CCa0(J)
    ENDIF
    Z2=CCa0(J)
    CCa0(J)=CCa0(J)-(dCdR-dCdRgoal)/(dCdR-dCdRold+TINY)*(CCa0(J)-
    & COLD(J))
    dCdRold=dCdR
    COLD(J)=Z2
    ENDIF

150 IF(ICa.GE.15.and.ICa.LT.25.OR.ICa.GE.35.AND.ICa.LT.45) THEN
    IF(IIC.EQ.0) THEN
        CCa0(J)=(.33+ICa/400.)*(Cmax-Cmin)+Cmin
        IIC=1
    ELSE
        CCa0(J)=(.67+ICa/400.)*(Cmax-Cmin)+Cmin
        IIC=0
    ENDIF
    ENDIF
    IF(CCa0(J).LE.Cmin) CCa0(J)=(.4+ICa/126.)*(Cmax-Cmin)+Cmin
    IF(CCa0(J).GE.Cmax) CCa0(J)=(.7+ICa/170.)*(Cmax-Cmin)+Cmin
    IF(CCa0(J).EQ.CCa0old) CCa0(J)=(.5-ICa/400.)*(Cmax-Cmin)+Cmin
    IF(CCa0(J).EQ.Z) CCa0(J)=(.6-ICa/400.)*(Cmax-Cmin)+Cmin

    IF(ICa.EQ.49) THEN
        DO 550,MM=M,MStart(J),-1
        IF(ShellFlux(J,MM).LT.0) THEN
            MStart(J)=MStart(J)+1
            MINUS=1
            GO TO 10
        ENDIF
    CONTINUE
550 ENDIF

    CCa0old=Z
    GO TO 199

201 CONTINUE
    IF(IFlux(J).EQ.1.AND.SolFrac(J,1).GT..95*PACK) THEN
        ShellFlux(J,M)=-4*RO**2*(dCdR*Dlime-ER*C/55334)
    ELSE
        ShellFlux(J,M)=-4*RO**2*dCdR*Dlime
    ENDIF

```

C Find shell where calculated flux is negative (due to evaporation) and

C begin again at next larger shell. If one isn't found, begin again at
 C the next smaller shell until a negative flux is found (MINUS is than
 C set to 1) and calculate final profile.

```

DO 300,MM=NStart(J),MStart(J),-1
IF(ShellFlux(J,MM).LT.0) THEN
  MStart(J)=MM+1
  IF(MStart(J).GT.NStart(J)) MStart(J)=NStart(J)
  MINUS=1
  GO TO 10
ENDIF
300 CONTINUE
IF(MStart(J).NE.1.AND.MINUS.EQ.0) THEN
  MStart(J)=MStart(J)-1
  GO TO 10
ENDIF

R=0
RR=0
DO 110,MM=1,MStart(J)-1
ShellFlux(J,MM)=0
R=R+dR(J,MM)
110 RR=RR+dR(J,MM)

M=MStart(J)-1
ICOUNT=0
IF(IPZ.EQ.1) PRINT *, 'R=',ZZZ,'L=',NZZ,' Ca=',CCaO(J)
&      , ' dCdR=',ZZZ
DO 210,L=1,NCa
ICOUNT=ICOUNT+1
IF(L/FLOAT(IN)-INT(L/IN).LT..01) ICOUNT=0
IF(ICOUNT.EQ.1) THEN
  M=M+1
  IF(M.NE.NStart(J)) THEN
    xdR=dR(J,M)/IN
  ELSE
    xdR=(R0-RR)/IN
  ENDIF
  RR=RR+dR(J,M)
ENDIF
R=R+xdR
IF(IPZ.EQ.1) PRINT *, 'R=',r,'L=',l,' Ca=',CCa(L)
&      , ' dCdR=',dcdr
210 CONTINUE
RETURN
END

```

FUNCTION CaDif(C,dCdR,R,J,M,VRR,ER)

C Second order differential equation governing diffusion of SO2
C the droplet or agglomerate.

REAL W(7,15),WPD(15,50),NPART(15,50)
REAL SolFrac(15,50)
REAL *8 R,C,dCdR
INTEGER Mevap(15),IFlux(15)

COMMON/DUM/W,WPD
COMMON/SA/RoughK
COMMON/LIME/Dlime,ClimeEq
COMMON/AG/DissRate,RateK,Dprod
COMMON/NPDR/NPart
COMMON/E/SD,PDO,SP,PDD
COMMON/MEVAP/Mevap
COMMON/SOL/SolFrac
COMMON/MOLD/Mold
COMMON/CLEDUM/CLEdum
COMMON/IF/IFlux
COMMON/PACK/PACK
common/dis/dis

IF(M.NE.Mold) Rough=1+EXP(Roughk*((WPD(J,M)/PDO)**3-.8))

C Liquid phase mass transfer.

IF(WPD(J,M).GT.0) THEN

IF(M.NE.Mold.OR.J.NE.Jold) THEN
EP=NPART(J,M)/1.3333333/VRR
Delta=(1/SolFrac(J,M)**.333333-1)
IF(Delta.GT.1) Delta=1
Delta=Delta*WPD(J,M)/2
CC=EP/(1-SolFrac(J,M))/(Dlime/Rough/DissRate/WPD(J,M)**2+
& (2/WPD(J,M)-1/(WPD(J,M)/2+Delta))/4)
ENDIF

ELSE
CC=0
ENDIF

A=CC
B=0
IF(R.NE.0) THEN
B=2*Dlime/R
IF(IFlux(J).EQ.1.AND.SolFrac(J,M).GT..95*PACK) A=A+2*ER/55334/R
ENDIF
IF(IFlux(J).EQ.1.AND.SolFrac(J,M).GT..95*PACK) B=B-ER/55334

CaDif=-CC*CLEDUM+A*C-B*dCdR

Mold=M
Jold=J
RETURN
END

1/2

SUBROUTINE PRINT(Dist,VAR,PD,ID,IA)

C Print results.

```
REAL CDO(15),DropNFlux(15),DropDiam(15),PD(15,50),NPart(15,50)
REAL VAR(7,15),WF(15),MWGO,DTime(15),MolWt,DsSolids(15)
REAL dR(15,50)
real CP(15,0:51),r0(15)
REAL *8 Dist
INTEGER ISTOP(15),NSHELL(15),nstart(15)
CHARACTER *1 Slu
```

```
COMMON/RKPR/NW,NE
COMMON/P/CDO,SMFO
COMMON/I/ISTOP
COMMON/E/SD,PD0,SP,PDD
COMMON/T/Time
COMMON/Y/SO2MF0
COMMON/PP/P
COMMON/FN/DropNFlux,DuctArea,AirMassFlux,WVMFlux0
COMMON/DROP/DropDiam
COMMON/WF/WF
COMMON/VOL/VolMol,CaUt
COMMON/CO2/CO2,MWGO
COMMON/SLU/Slu
COMMON/CAS/CaS
COMMON/DTIME/DTime
COMMON/TO/TO
COMMON/DS/DsSolids
COMMON/NS/NSHELL
COMMON/NPDR/NPart
COMMON/DR/dR
COMMON/MOL/MolWt
COMMON/ASH/ASHFLUX0,DASH,ASHFLUX
COMMON/UTO/UTO,EFFCAS,PDRO
COMMON>IDRY>IDRY
COMMON/PRE/PRECYCLE
COMMON/IHED/IHED
common/emt/emratio
common/CP/cp
common/nt/nstart
```

C Calculate captured Sorbent Mass Flux, Water Vapor Mass Flux, fraction
C water unevaporated (XW), SO2 Mass Flux captured, water mole fraction
C in the bulk gas phase (YG), and SO2 capture (Cap).

```
XW=0
SMF=0
WVMFlux=WVMFlux0
Util=0
SO2MF=0
NUM=NW
DO 59,I=1,NW
```

```

      IF(Slu.NE.'S'.OR.Slu.NE.'D') SMF=SMF+DropNFlux(I)*VAR(2,I)/6
&      *3.14159*(1-SP)*SD*PDD**3
      WVMFlux=WVMFlux+DropNFlux(I)*CDO(I)*(1-VAR(5,I))
      XW=XW+WF(I)*VAR(5,I)
      IF(ISTOP(I).EQ.1) NUM=NUM-1
      DUM=0
      DUM2=0
      IF(VAR(2,I).LE.0) GO TO 59
      DO 205,M=1,NSHELL(I)
      IF(Slu.NE.'D') THEN
        DUM=DUM+NPart(I,M)*(PDD**3-PD(I,M)**3)
        DUM2=DUM2+NPart(I,M)*(PDO**3-PD(I,M)**3)
      ELSE
        IF(I.EQ.1) THEN
          DUM=DUM+(PDO**3-PD(I,M)**3)
        ELSE
          DUM=DUM+(PDRO**3-PD(I,M)**3)
        ENDIF
        DUM2=DUM2+(PDO**3-PD(I,M)**3)
      ENDIF
205    CONTINUE
      Util=Util+DUM2/VAR(2,I)*WF(I)
      SO2MF=SO2MF+DropNFlux(I)/(1.90986/(1-SP))/VolMol*(1-CaUt)
&      *DUM
59    CONTINUE

      IF(Slu.EQ.'D') THEN
        WVMFlux=WVMFlux0-CDO(1)*VAR(5,1)*DropNFlux(1)
        XW=VAR(5,1)*CDO(1)/(3.14159*PDO**3/6*(1-SP))*VolMol/18
      ENDIF
      Cap=SO2MF/SO2MFO
      Util=Util/PDO**3

```

C Calculate the water mole fraction in the gas phase (XO), the
 C saturation temperature (TSat), and the approach to saturation (ASat).

```

      XO=WVMFlux/18/(WVMFlux/18+AirMassFlux/MWGO)
      TSat=46.13+3816.44/(18.3036-ALOG(XO*P*760))
      ASat=(VAR(1,1)*T0)-TSat

```

C Print the results.

```

      IF(SO2MFO.EQ.0.OR.SMFO.EQ.0) THEN
        PRINT 15,Dist,Time,XW,(VAR(1,1)*T0),ASat,NUM,XO
        WRITE(9,15) Dist,Time,XW,(VAR(1,1)*T0),ASat,NUM,XO
      ELSEIF(Slu.EQ.'D') THEN
        IF(ID.EQ.0) THEN
          IF(CAP.LT..02) THEN
            PRINT 11,Dist,Time,XW,Util*100,Cap*100
            WRITE(9,11) Dist,Time,XW,Util*100,Cap*100
          ELSE
            PRINT 10,Dist,Time,XW,Util*100,Cap*100
            WRITE(9,10) Dist,Time,XW,Util*100,Cap*100
          ENDIF
        ELSE
          PRINT 10,Dist,Time,XW,Util*100,Cap*100
          WRITE(9,10) Dist,Time,XW,Util*100,Cap*100
        ENDIF
      ENDIF

```

```

ENDIF
IF(IDRY.EQ.1.AND.ID.EQ.0) THEN
  ID=1
ELSEIF(IDRY.EQ.1) THEN
  IF(CAP.LT..02) THEN
    PRINT 21,Dist,Time,Util*100,Cap*100
    WRITE(9,21)Dist,Time,Util*100,Cap*100
  ELSE
    PRINT 20,Dist,Time,Util*100,Cap*100
    WRITE(9,21) Dist,Time,Util*100,Cap*100
  ENDIF
ENDIF
ELSEIF(Slu.EQ.'S') THEN
  IF(CAP.LT..02) THEN
    PRINT 11,Dist,Time,XW,Util*100,Cap*100,(VAR(1,1)*TO),ASat
    &      ,NUM,XO
    WRITE(9,11) Dist,Time,XW,Util*100,Cap*100,(VAR(1,1)*TO),ASat
    &      ,NUM,XO
  ELSE
    PRINT 10,Dist,Time,XW,Util*100,Cap*100,(VAR(1,1)*TO),ASat
    &      ,NUM,XO
    WRITE(9,10) Dist,Time,XW,Util*100,Cap*100,(VAR(1,1)*TO),ASat
    &      ,NUM,XO
  ENDIF
c  print *, 'EmtRatio = ', emratio
ELSE
  IF(IHED.EQ.0) THEN
    PRINT 11,Dist,Time,XW,SMF/SMFO*100,Cap*100,(VAR(1,1)*TO),ASat
    &      ,NUM,XO
    WRITE(9,11)Dist,Time,XW,SMF/SMFO*100,Cap*100,(VAR(1,1)*TO),
    &      ASat,NUM,XO
  ELSE
    PRINT 10,Dist,Time,XW,Util*100,Cap*100,(VAR(1,1)*TO),ASat
    &      ,NUM,XO
    WRITE(9,10) Dist,Time,XW,Util*100,Cap*100,(VAR(1,1)*TO),ASat
    &      ,NUM,XO
  ENDIF
ENDIF
11  FORMAT(F7.2,1X,F6.3,4X,F5.3,4X,F6.2,4X,F6.3,4X
&      ,F5.1,3X,F5.1,2X,I5,4X,F4.3,4X,F5.2)
10  FORMAT(F7.2,1X,F6.3,4X,F5.3,4X,F6.1,4X,F6.2,4X
&      ,F5.1,3X,F5.1,2X,I5,4X,F4.3,4X,F5.2)
15  FORMAT(F7.2,4X,F6.3,7X,F5.3,10X,F5.1,6X,F5.1,5X,I5,7X,F5.4)

21  FORMAT(F7.2,1X,F6.3,5X,' " ',5X,F6.2,4X,F6.3,4X
&      ,F5.1 3X,F5.1,2X,I5,4X,F5.4,4X,F6.2)
20  FORMAT(F7.2,1X,F6.3,5X,' " ',5X,F6.1,4X,F6.2,4X
&      ,F5.1,3X,F5.1,2X,I5,4X,F5.4,4X,F6.2)

```

C Optional printout of drop size distribution either when called for
C or at the end of the duct.

```

      IF(IA.EQ.0) THEN
      PRINT *
      PRINT 77,'At ',Dist,' meters the individual drop parameters are:
&
      PRINT *
77  FORMAT(A13,F7.3,A)
      IF(Slu.NE.'D') THEN
      PRINT *, 'Drop Diam  Frac Water  %Water',
& ' Drop Temp  Drop Time  Drop Vel  % Util  %Ash'

C Calculate the mass of solids in each drop, SMass, the cumulative
C capture of the large drops, and weighted cumulative capture
C of the large drops.

      DO 111,I=NW,1,-1
      DUM=0
      DUM2=0
      DO 5,M=1,NSHELL(I)
      DUM2=DUM2+(1-(PD(I,M)/PDO)**3)*NPart(I,M)
5  DUM=DUM+((PDO**3-PD(I,M)**3)*129/MolWt+PD(I,M)**3)*NPart(I,M)
      ASHMASS=3.14159/6*SD*DASH**3*VAR(3,I)
      SMass=3.14159/6*SD*(1-SP)*DUM+DsSolids(I)+ASHMASS
      DUM2=DUM2/VAR(2,I)*100

111 PRINT 12,DropDiam(I)*1E6,VAR(5,I)*WF(I)
& ,VAR(5,I)*CDO(I)/(VAR(5,I)*CDO(I)+SMass)*100,(VAR(6,I)*TO),
& DTime(I),VAR(4,I),DUM2,ASHMASS/(SMass+VAR(5,I)*CDO(I))
& *100

12  FORMAT(2X,F7.2,6X,F5.3,5X,F6.2,5X,F5.1,5X,F7.4,4X,F6.2,4X,F6.2,
& 2X,F4.1,3X,F5.1)
      PRINT *

      ELSE
      PRINT*, 'Particle Diameter      Core Diameter'
      PRINT*, '      (microns)      (microns)      % Utilization'
      DO 118,I=1,NW
      DUM2=(1-(PD(I,1)/PDO)**3)*100
118 PRINT 119,DropDiam(I)*1E6,PD(I,1)*1E6,DUM2
      PRINT *
      ENDIF
119 FORMAT(5X,F6.2,16X,F6.2,13X,F6.2)

      ENDIF

      RETURN
      END

```


APPENDIX 2

MAJOR MODEL VARIABLES

A2.1 Variables Common Throughout Model

AirMassFlux = Mass flux of dry air ($\text{g}/\text{m}^2 \cdot \text{s}$)

ALPHA = Ratio of calcium sulfite molar volume to calcium hydroxide molar volume

ASat = Approach to saturation (K)

AshFlux = Flux of ash through duct ($\text{g}/\text{m}^2 \cdot \text{s}$)

AshFlux0 = Initial flux of ash through duct ($\text{g}/\text{m}^2 \cdot \text{s}$)

CaS = Calcium to sulfur molar ratio

CaUt = Fraction of calcium initially utilized by sulfur. For use when boiler injection is followed by a scavenging spray

CO2 = Dry CO2 molar fraction

CO20 = Molar fraction of CO2 initially in the duct gases (wet basis)

CDO(I) = Initial mass of water in a drop (g)

DASH = Diameter of ash particles (m)

DAVE = Allows the velocity of different sized drops to be entered independently. Entered either as Yes or No

DissRate = k_d in Eq. 13

Dist = Distance down duct (m)

DHum = Molar fraction of water initially in the duct gases

DIR = Direction of flow in duct. Entered as Up, Down, or Horizontal

dR(I,M) = Size of differential radial shells (m)

Dprod = D_s in Eqs. 17 and 22

DropNFlux(I) = the number flux of drops of each size ($\#/\text{m}^2 \cdot \text{s}$)

DropDen0 = Initial density of the drop, gm/m^3

DropDens = Slurry drop density (g/m^3)

DropDiam(I) = Diameter of drop (m)

DropTemp = Initial temperature of drops (K)

dRSO2(I) = Distance SO_2 penetrates into drop (m)

DsSolids(I) = Mass of dissolved solids in a drop (g)

DTime(I) = Drop time of individual drops (s)

DuctArea = Cross sectional area of duct (m^2)

Duct Length = Length of duct (m)

EFFCAS = Effective calcium to sulfur ratio (due to recycle)

FILEIN = Current data file

GasFlowRate = Duct flow rate (m^3/s)
 GasMassRate = Mass flow rate of gases initially in the duct (Kg/s)
 GV = Duct gas velocity (m/s)
 IDRY(I) = Stores when a dry sorbent particle injected into a pre-humidified duct has reached the duct temperature
 IFlux(I,M) = 1 when the fraction of solids is high enough in an outer radial shell so that a flux of water (due to evaporation) is present
 IMIN = Smallest drop not evaporated
 ISTOP(I) = 1 when a drop has evaporated
 IVSTOP(I) = 1 when a drop has decelerated to the duct gases velocity
 IWARN = Sends message to DEC.FOR when spray has evaporated, program has diverged, etc.
 H = Step size in duct (m)
 Meavp(I) = 1 if drop has evaporated
 MolWt = Molecular weight of the sorbent (g/mole)
 MWGO = Molecular weight of the duct gas exclusive of water vapor (g/mole)
 NASH(I,M) = Number of ash particles at a radial location
 NASHOLD(I) = Number of ash particles in a droplet from the previous time step
 NE = Number of differential Equations to be solved in FNC
 NShell(I) = Number of radial shells considered in a drop
 NPart(I,M) = Number of sorbent particles in a radial shell
 NPartOld(I,M) = Save number of sorbent particles in a radial shell
 NStart(I) = Radial shell from where the initial SO_2 concentration will be solved
 NSTEPS = Number of times RUNGEKUTT is called, used to calculate a running average drop temperature which is used to determine when a slurry droplet has dried
 NW = Number of drop sizes contained in the spray size distribution
 P = Pressure of duct (atm)
 PD(I,M) = Sorbent Particle Diameter (m)
 PDD = Initial average sorbent particle diameter for slurry injection and dry injection followed by a spray cases (m)
 PDO = Initial sorbent particle diameter (m)
 PDR0 = Initial diameter of recycled sorbent for humidification followed by dry injection (m)

PPM = ppm SO₂ in duct gases
 PRECYCLE = Fraction of sorbent recycled
 PSDPt = Indicates when drop variables are to be printed (m)
 RateK = k_r in Eqs. 17 and 22
 RdryO(I,M) = Radius of sorbent particle when slurry drop dried (m)
 RoughK = Roughness factor to account for the loss of BET surface area as the reaction proceeds
 RWCore(I) = Radius of water in agglomerate (m)
 SD = Sorbent density (gm/m³)
 ShellFlux(I,M) = Molar flux of sulfur or calcium through a radial shell (moles/m².s)
 Slu = Indicates whether sorbent is present in the spray as a slurry(S) as a Dry particle injected into a pre-humidified duct (D), or as a particle which will be scavenged by a spray (any letter but D or S)
 SluConc = Slurry Concentration (weight fraction)
 SMFO = Initial sorbent mass flux in the duct (g/m².s)
 SO2MFO = Initial molar flux of SO₂ (mole/m².s)
 SolFrac(I,M) = Fraction of solids in a radial position
 SP = Sorbent porosity. Usually entered as 0 for hydrated lime
 SurfArea = Surface area of sorbent (m²/g). Default value of 15 used if 0 entered
 Tave = Running average drop temperature which is used to determine when a slurry droplet has dried (K)
 Time = Residence time for the duct gases (s)
 T0 = Initial temperature of duct gases (K)
 UTO = Initial average utilization of sorbent (due to recycle)
 VAR(1,1) = Gas Temperature
 VAR(2,1) = Number of sorbent particles in a drop (#)
 VAR(3,1) = Individual Drop Velocity (m/s)
 VAR(4,1) = Average sorbent diameter in a drop (m)
 VAR(5,1) = Mass water remaining in drop
 VAR(6,1) = Individual Drop temperature (K)
 VolFrac = Fraction of the slurry drop occupied by sorbent
 VolMol = Molar volume of the sorbent (m³/mole)

W(1-6,I) = VAR(1-6,I), varies in RUNGKUTT and subsequent subroutines
WaterVel = Velocity of spray (m/s)
WF(I) = Weight Fraction of each size of drops in the total spray. Sum of
entered WF(I) should equal 1
WMRO = Rate of spray into duct (g/s)
WPD(I,M) = PD(I,M), varies in RUNGKUTT
WVMFlux0 = Initial water vapor mass flux, (g/m²·s)
Y0 = Initial molar fraction of SO₂ in the duct gases

A2.2 Variables Specific to Subroutines

DEC.FOR

ICLK = Determiner when print step size should be changed

PRNTSTP = Print step size

RUNGKUTT.FOR

HMIN = H in DEC.FOR

K(L,J,M) = Runge-Kutta values

KPD(L,J,M) = Runge-Kutta values for particle size

PHY.FOR

Cf = Concentration of gases in film around drop (moles/m³)

Cg = Concentration of gases in the duct (moles/m³)

CMTW = Coefficient of mass transfer of water to drop (mole/m².s)

Conda = Thermal conductivity of air (J/m.s.°C)

Condf = Thermal conductivity of film surrounding drop (J/m.s.°C)

CondW = Thermal conductivity of water vapor (J/m.s.°C)

CpA = Heat capacity of air (J/mol.°C)

CpCO2 = Heat capacity of CO2 (J/g.°C)

CpW = Heat capacity of water vapor (J/mol.°C)

D2 = Drop diameter squared (m²)

D3 = Drop diameter squared (m³)

DenF = Molar density of gases surrounding drop (moles/m³)

Dmin = Minimum diameter of drop before water recedes below surface (m)

Dv = Diffusivity of water vapor (m²/s)

GasMassFlux = Mass flux of gases in the duct (g/m².s)

HTC = Heat transfer coefficient (J/m².s)

MuAir = Viscosity of air (g/m.s)

MuW = Viscosity of water vapor (g/m.s)

MWF = Molecular weight of gases in the film surrounding drop (g/mole)

MWG = Molecular weight of gases in the duct (g/mole)
 Nu = Nusselt Number
 Pr = Prandtl Number
 Re = Reynolds Number based on film properties
 Reg = Reynolds Number based on duct gas properties
 Sc = Schmidt Number
 Sh = Sherwood Number
 SMass = Mass of solids in a drop (g)
 SO2MFlux = Mass flux of SO₂ in duct gases (moles/m².s)
 Tc = Temperature in °C
 Td = Drop temperature (K)
 Tf = Film temperature around drop (K)
 Tg = Gas temperature (K)
 VisG = Viscosity of duct gases (g/m.s)
 WVMFlux = Gas phase water vapor mass flux (moles/m².s)
 XF = Mole fraction of water vapor in the film surrounding drop
 XG = Mole fraction of water vapor in duct
 XO = Mole fraction of water vapor at the drop surface
 YF = Mass fraction of water vapor in the film surrounding drop
 YG = Mass fraction of water vapor in duct
 YS8 = Mole fraction of SO₂ in the duct gases

PHY.FOR AND FNC.FOR

CpW = Heat capacity of water vapor (J/g.°C)
 DeltaV = Velocity difference between drop and duct gases (m/s)
 DenG = Density of duct gases (molar or mass basis)
 ER = Molar flux of water evaporating from a drop (moles/m²/s)
 ERate = Moles of water evaporating from a drop (moles/s)
 HtCapG = Heat capacity of duct gases (J/g.°C)
 HtCapF = Heat capacity of film surrounding drop (J/g.°C)
 HtCapW = Heat capacity of water (J/g.°C)
 HtVAP = Heat of vaporization of water (J/mole)
 Q = Heat flow to a drop (J/s)

RE = Reynold's Number based on film properties

SMF = Sorbent mass flux in gas phase

FLX.FOR, PHY.FOR, DIFF.FOR, CADIF.FOR

ClimeEq = Equilibrium concentration of lime in water (moles/m³)

CMTSO2 = Mass transfer coefficient of SO₂ to drop i (mole/m².s)

DHSO3 = Diffusivity of HSO₃⁻ (m²/s)

DH2SO3 = Diffusivity of H₂SO₃ (m²/s)

DSO2 = Diffusivity of SO₂ in gas phase (m²/s)

Dlime = Diffusivity of lime in water (m²/s)

HE = Henry's Constant

KDISSOC = Dissociation constant of H₂SO₃ (mole/m³)

YS8 = Mole fraction of SO₂ in the gas phase

FLX.FOR

CO(I) = SO₂ concentration at drop center (mole/m³)

Cold1 = Stored CO (mole/m³)

dCdR = Change in liquid phase sulfur concentration divided by the change in radius

IDIV2 = Records when SO₂ diffusion to the drop center has been tried

IDiverge = Number of iterations

R = Radius used in liquid phase sulfur diffusion calculations (m)

RO(I) = Radius at which liquid phase sulfur concentrations drop to zero (m)

Rmin = Minimum RO which gave incorrect value (m)

Rmax = Maximum RO which gave incorrect value (m)

Rold1(I) = Stored RO (m)

RR = Outer radius of radial shell (m)

VRR = Volume of radial shell (m³)

XS = SO₂ mole fraction at the drop surface

YS8CALC = Calculated gas phase SO₂ mole fraction

YS8OLD = Stored calculated gas phase SO₂ mole fraction

DIFF.FOR

DEL = Film thickness around a sorbent particle (m)

EP = Concentration of sorbent particles in radial shell ($\#/m^3$)

CA.FOR

CCaO(I) = Liquid phase calcium concentration at drop center (mole/m^3)

Cmin = Minimum CCaO which gave incorrect value (mole/m^3)

Cmax = Maximum CCaO which gave incorrect value (mole/m^3)

ICa = Iterations

IMAX = Maximum total number of iterations

IN = Number of differential elements in each radial shell used in calculating
Ca diffusion

R = Radius used in liquid phase sulfur diffusion calculations (m)

RR = Outer radius of radial shell (m)

VRR = Volume of radial shell (m^3)

CADIF.FOR

Delta = Film thickness around a sorbent particle (m)

SUL.FOR

EP = Concentration of sorbent particles in radial shell ($\#/m^3$)

Rs3 = Radius of sorbent particle divided by the radius of the unreacted core,
quantity cubed (m^3)

XS = SO_2 mole fraction at the drop surface

XW = Mass fraction of water on sorbent particle

PRD.FOR

ASat = Approach to saturation ($^{\circ}C$)

Cap = Fraction SO_2 capture

NUM = Number of drops which have not evaporated
SMass = Mass of solids in a drop (g)
SMF = Sorbent mass flux in the gas phase ($\text{g}/\text{m}^2 \cdot \text{s}$)
SO2MF = Mole flux of SO_2 captured ($\text{g}/\text{m}^2 \cdot \text{s}$)
TSat = Dew point (K)
Util = Average utilization of sorbent in the spray
WVMFlux = Gas phase water vapor mass flux ($\text{g}/\text{m}^2 \cdot \text{s}$)
XO = Water mole fraction in the gas phase
XW = Fraction spray unevaporated

APPENDIX 3

RAW DATA TABLES

TABLE A3-1

<u>Experimental Parameter:</u>	Baseline Conditions
<u>Sorbent:</u>	Marblehead AH Bag 2
<u>Slurry Conc:</u>	20% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	CH ₄
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
03170789	127687	5 cm	390	303	390	303	32.41	32.41
02170789	127686	17 cm	760	1228	760	1228	67.41	67.41
01170789	127685	33 cm	320	504	320	504	65.71	65.71

TABLE A3-2

<u>Experimental Parameter:</u>	Baseline Conditions
<u>Sorbent:</u>	Marblehead AH Bag 4
<u>Slurry Conc:</u>	20% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	CH ₄
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
07130989	127903	Probe Capt	719	160	708	110	9.28	6.48
11130989	127907	Filter Capt	11	50	0	0	****	****
10130989	127906	5 cm	359	140	348	90	16.27	10.79
09130989	127905	17 cm	539	250	528	200	19.35	15.80
08130989	127904	33 cm	749	300	738	250	16.71	14.13
02260989	127852	Probe Capt	715	96	700	82	5.66	4.89
03260989	127853	Filter Capt	15	14	0	0	****	****
06260989	127856	5 cm	705	226	690	212	13.37	12.82
05260989	127855	17 cm	765	386	750	372	21.05	20.69
04260989	127854	33 cm	745	390	730	376	21.84	21.49
07260989	127857	4 cm	705	190	690	176	11.24	10.64
08260989	127770	3 cm	465	140	450	126	12.56	11.68
09260989	127701	2 cm	125	37	110	23	12.35	8.72

TABLE A3-3

<u>Experimental Parameter:</u>	Baseline Conditions
<u>Sorbent:</u>	Marblehead AH Bag 5
<u>Slurry Conc:</u>	20% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	CH ₄
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
02290989	127743	Probe Capt	598	90	596.2	80	6.28	5.60
03290989	127744	Filter Capt	1.8	10	0	0	****	****
06290989	127747	5 cm	568	240	566.2	230	17.63	16.95
05290989	127746	17 cm	608	360	606.2	350	24.70	24.09
04290989	127745	33 cm	678	370	676.2	360	22.77	22.21
02231089	128022	Probe Capt	440	92	434.9	39	8.72	3.74
02231089	128023	Filter Capt	5.1	53	0	0	****	****
06231089	128026	5 cm	640	230	634.9	177.00	14.99	11.63
05231089	128025	17 cm	600	320	594.9	267	22.25	18.72
04231089	128024	33 cm	510	380	504.9	327	31.09	27.02

TABLE A3-4

<u>Experimental Parameter:</u>	Baseline Conditions
<u>Sorbent:</u>	Marblehead AH Bag 6
<u>Slurry Conc:</u>	20% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	CH ₄
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
07231089	128027	Probe Capt	760	130	754	103	7.14	5.70
08231089	128028	Filter Capt	6	27	0	0	****	****
11231089	128031	5 cm	690	300	684	273	18.14	16.65
10231089	128030	17 cm	590	400	584	373	28.28	26.65

TABLE A3-5

<u>Experimental Parameter:</u>	Baseline Conditions
<u>Sorbent:</u>	Marblehead AH Bag 7
<u>Slurry Conc:</u>	20% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	H ₂
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
02070390	128906	Probe Capt	110	53	107.4	40	20.10	15.54
03070390	128907	Filter Capt	2.6	13	0	0	****	****
05070390	128909	17 cm	18	28	15.4	15	64.90	40.64
04070390	128908	33 cm	140	130	137.4	117	38.74	35.53

TABLE A3-6

<u>Experimental Parameter:</u>	Sorbent Type - quicklime
<u>Sorbent:</u>	Marblehead Quicklime
<u>Slurry Conc:</u>	20% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	H ₂
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
02251089	128033	Probe Capt	560	120	556.4	97	8.94	7.27
03251089	128034	Filter Capt	3.6	23	0	0	****	****
06251089	128037	5 cm	580	25	676.4	2	1.53	0.12
05251089	128036	17 cm	640	330	636.4	307	21.51	20.13
04251089	128035	33 cm	730	640	726.4	617	36.58	35.44

TABLE A3-7

<u>Experimental Parameter:</u>	Sorbent Type - special quicklime
<u>Sorbent:</u>	Marblehead hydrate, bag 7, carefully calcined under N ₂
<u>Slurry Conc:</u>	20% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	H ₂
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
02170490	128849	Probe Capt	340	120	336.2	110.7	14.72	13.74
03170490	128850	Filter Capt	3.8	9.3	0	0	****	****
06170490	128853	5 cm	350	260	346.2	250.7	30.99	30.21
05170490	128851	17 cm	550	510	546.2	500.7	38.69	38.24
04170490	128851	33 cm	350	430	346.2	420.7	51.26	50.7

TABLE A3-8

Experimental Parameter: Sorbent Type - alternate hydrate
Sorbent: Mississippi Hydrate
Slurry Conc: 20% wt-vol
SO₂ Conc: 1500 ppm
Fuel CH₄
Rotor Speed: 20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
02271089	128944	Probe Capt	420	120	416.1	94	11.92	9.42
03271089	128945	Filter Capt	3.9	26	0	0	****	****
06271089	128949	5 cm	490	280	486.1	254	23.84	21.80
05271089	128948	17 cm	590	500	586.1	474	35.36	33.74
04271089	128947	33 cm	540	440	536.1	414	33.99	32.22

TABLE A3-9

<u>Experimental Parameter:</u>	Sorbent Type - alternate quicklime
<u>Sorbent:</u>	Mid-Ohio Valley quicklime
<u>Slurry Conc:</u>	20% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	CH ₄
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
02301089	128951	Probe Capt	521	120	516	106	9.63	8.57
03301089	128952	Filter Capt	4	14	0	0	****	****
06301089	128955	5 cm	490	270	486	256	22.99	21.98
05301089	128954	17 cm	690	500	686	486	30.23	29.56
04301089	128953	33 cm	560	380	556	366	28.31	27.46

TABLE A3-10

<u>Experimental Parameter:</u>	Slurry Concentration
<u>Sorbent:</u>	Marblehead AH Bag 2
<u>Slurry Conc:</u>	1% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	CH ₄
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
11200789	127717	5 cm	50	140	50	140	116.82	116.82
10200789	127718	17 cm	71	160	71	160	94.02	94.02
08200789	127719	33 cm	110	220	110	220	83.44	83.44

TABLE A3-11

Experimental Parameter: Slurry Concentration
Sorbent: Marblehead AH Bag 2
Slurry Conc: 2% wt-vol
SO₂ Conc: 1500 ppm
Fuel CH₄
Rotor Speed: 20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
05200789	127722	5 cm	86	140	86	140	67.92	67.92
06200789	127721	17 cm	160	250	160	250	65.19	65.19
07200789	127720	33 cm	160	250	160	250	65.19	65.19

TABLE A3-12

Experimental Parameter: Slurry Concentration
Sorbent: Marblehead AH Bag 2
Slurry Conc: 5% wt-vol
SO₂ Conc: 1500 ppm
Fuel CH₄
Rotor Speed: 20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO4 mg/L	Ca corr.	SO4 corr.	Ca util. meas. Percent	Ca util. corr. Percent
04210789	127713	Filter Capt	11	23	0	0	****	****
01200789	127723	5 cm	100	110	89	87	45.89	40.78
02200789	127724	17 cm	240	320	229	297	55.63	54.11
03200789	127725	33 cm	240	370	229	347	64.32	63.22

TABLE A3-13

Experimental Parameter: Slurry Concentration
Sorbent: Marblehead AH Bag 2
Slurry Conc: 10% wt-vol
SO₂ Conc: 1500 ppm
Fuel CH₄
Rotor Speed: 20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
03190789	127729	5 cm	180	180	180	180	41.72	41.72
02190789	127730	17 cm	160	250	160	250	65.19	65.19
01190789	127697	33 cm	110	190	110	190	72.06	72.06

TABLE A3-14

Experimental Parameter: Slurry Concentration
Sorbent: Marblehead AH Bag 2
Slurry Conc: 30% wt-vol
SO₂ Conc: 1500 ppm
Fuel CH₄
Rotor Speed: 20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
04170789	127688	5 cm	550	410	550	410	31.10	31.10
05170789	127689	17 cm	420	480	420	480	47.68	47.68
06170789	127690	33 cm	940	1200	940	1200	53.26	53.26

TABLE A3-15

<u>Experimental Parameter:</u>	Drops/size/rotor speed
<u>Sorbent:</u>	Marblehead AH Bag 4
<u>Slurry Conc:</u>	20% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	CH ₄
<u>Rotor Speed:</u>	10 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
02180989	127916	Probe Capt	114	38	108	5	13.91	1.93
06180989	127699	Filter Capt	6	33	0	0	****	****
05180989	127919	5 cm	164	87	158	54	22.13	14.26
04180989	127918	17 cm	124	77	118	44	25.91	15.56
03180989	127917	33 cm	134	66	128	33	20.55	10.76

TABLE A3-16

Experimental Parameter: SO₂ Concentration
Sorbent: Marblehead AH Bag 3
Slurry Conc: 20% wt-vol
SO₂ Conc: 100 ppm
Fuel CH₄
Rotor Speed: 20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
01090889	127883	Probe Capt	390	83	385.3	72	8.88	7.80
05090889	127879	Filter Capt	4.7	11	0	0	****	****
06090889	127878	5 cm	420	48	415.3	37	4.77	3.72
03090889	127881	17 cm	410	46	405.3	35	4.68	3.60
04080889	127880	33 cm	410	51	405.3	40	5.19	4.12

TABLE A3-17

<u>Experimental Parameter:</u>	SO ₂ Concentration
<u>Sorbent:</u>	Marblehead AH Bag 3
<u>Slurry Conc:</u>	20% wt-vol
<u>SO₂ Conc:</u>	500 ppm
<u>Fuel</u>	CH ₄
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
08030889	127889	Probe Capt	210	90	198	50	17.88	10.54
06030889	127885	Filter Capt	12	40	0	0	****	****
05030889	127886	5 cm	210	120	198	80	23.84	16.86
04030889	127887	17 cm	370	320	358	280	36.08	32.63
03130989	127888	33 cm	380	320	368	280	35.13	31.74

TABLE A3-18

Experimental Parameter: SO₂ Concentration
Sorbent: Marblehead AH Bag 4
Slurry Conc: 20% wt-vol
SO₂ Conc: 5000 ppm
Fuel CH₄
Rotor Speed: 20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO4 mg/L	Ca corr.	SO4 corr.	Ca util. meas. Percent	Ca util. corr. Percent
02130989	127898	Probe Capt	485	250	480.3	190	21.51	16.50
06130989	127902	Filter Capt	4.7	60	0	0	****	****
05130989	127901	5 cm	435	280	430.3	220	26.85	21.33
04130989	127900	17 cm	735	550	730.3	490	31.22	27.99
03130989	127899	33 cm	815	620	810.3	560	31.74	28.83

TABLE A3-19

<u>Experimental Parameter:</u>	Sorbent Surface Area
<u>Sorbent:</u>	50 m ² /g methanol hydrate
<u>Slurry Conc:</u>	16% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	CH ₄
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
06240789	127704	Probe Capt	400	68	389	45	7.09	4.83
05240789	127705	Filter Capt	11	23	0	0	****	****
04240789	127706	5 cm	720	440	709	417	25.50	24.54
03240789	127707	17 cm	680	590	669	567	36.20	35.36
01240789	127709	33 cm	690	650	679	627	39.3	38.52

TABLE A3-20

<u>Experimental Parameter:</u>	Influence of methanol
<u>Sorbent:</u>	Marblehead AH Bag 5
<u>Methanol Conc:</u>	1.25% vol/vol in hydration water
<u>Slurry Conc:</u>	20% wt-vol before methanol addition
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	CH ₄
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas Percent	Ca util. corr. Percent
04270989	127737	Probe Capt	800	160	797.6	138	8.34	7.22
05270989	127738	Filter Capt	2.4	22	0	0	****	****
08270989	127741	5 cm	740	270	737.6	248	15.22	14.03
07270989	127740	17 cm	890	430	887.6	408	20.16	19.18
06270989	127739	33 cm	860	430	857.6	408	20.86	19.85

TABLE A3-21

<u>Experimental Parameter:</u>	Influence of methanol
<u>Sorbent:</u>	Marblehead AH Bag 5
<u>Methanol Conc:</u>	4.75% vol/vol in hydration water
<u>Slurry Conc:</u>	20% wt-vol before methanol addition
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	CH ₄
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
07290989	127748	Probe Capt	578	86	576.5	72	6.21	5.21
08290989	127749	Filter Capt	1.5	14	0	0	****	****
11290989	127763	5 cm	558	236	556.5	222	17.65	16.64
10290989	127696	17 cm	608	356	606.5	342	24.43	23.53
09290989	127750	33 cm	618	346	616.5	332	23.36	22.47

TABLE A3-22

<u>Experimental Parameter:</u>	Effect of CO ₂ / fuel type
<u>Sorbent:</u>	Marblehead AH Bag 4
<u>Slurry Conc:</u>	20% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	H ₂
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
07150989	127914	Probe Capt	581	158	562	96	11.35	7.13
06150989	127913	Filter Capt	19	62	0	0	****	****
05150989	127912	5 cm	551	198	532	136	14.99	10.67
04150989	127911	17 cm	761	508	742	446	27.85	25.08
03150989	127910	33 cm	511	328	492	266	26.78	22.56

TABLE A3-23

Experimental Parameter: Relative humidity
Sorbent: Marblehead AH Bag 2
Relative Humidity: near 0%
Slurry Conc: 20% wt-vol
SO₂ Conc: 1500 ppm SO₂
Fuel CH₄
Rotor Speed: 20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
05210789	127712	Probe Capt	1000	78	996.7	72	3.25	3.01
04210789	127713	Filter Capt	3.3	6	0	0	****	****
01210789	127716	5 cm	610	310	606.7	304	21.20	20.90
02210789	127715	17 cm	850	440	846.7	434	21.60	21.38
03210789	127714	33 cm	1000	480	996.7	474	20.03	19.84

TABLE A3-24

<u>Experimental Parameter:</u>	SO ₂ introduced at probe entrance/probe capture
<u>Sorbent:</u>	Marblehead AH Bag 4
<u>Slurry Conc:</u>	20% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	CH ₄
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
01090889	127848	Probe Capt	623	133	616.3	116	8.91	7.85
05090889	127847	Filter Capt	6.7	17	0	0	****	****

TABLE A3-25

<u>Experimental Parameter:</u>	Water spray during probe capture
<u>Sorbent:</u>	Marblehead AH Bag 4
<u>Slurry Conc:</u>	20% wt-vol
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	CH ₄
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
13210989	127842	Probe Capt	655	110	655	110	7.01	7.01

TABLE A3-26

Experimental Parameter: Probe Capture Test, Baseline Conditions
Sorbent: Marblehead AH Bag 4
Slurry Conc: 20% wt-vol
SO₂ Conc: 1500 ppm
Fuel CH₄
Rotor Speed: 20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
08210989	127837	17 cm	628	317	628	317	21.06	21.06

TABLE A3-27

<u>Experimental Parameter:</u>	Promotor effect
<u>Sorbent:</u>	Marblehead AH Bag 7
<u>Promotor:</u>	Acetic Acid
<u>Promotor Conc:</u>	10 mol - % rel. to calcium
<u>Slurry Conc:</u>	20% wt-vol before promotor addition
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	H ₂
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
01020390	128975	Probe Capt	120	40	117.7	26	13.91	9.22
04020390	128977	Filter Capt	2.3	14	0	0	****	****
06020390	128980	5 cm	110	65	107.7	51	24.65	19.76
05020390	128979	17 cm	240	200	237.7	186	34.77	32.65
03020390	128987	33 cm	220	220	217.7	206	41.72	39.48

TABLE A3-28

<u>Experimental Parameter:</u>	Promotor effect
<u>Sorbent:</u>	Marblehead AH Bag 7
<u>Promotor:</u>	Formic Acid
<u>Promotor Conc:</u>	10 mol - % rel. to calcium
<u>Slurry Conc:</u>	20% wt-vol before promotor addition
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	H ₂
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
08070390	128910	Probe Capt	190	49	187.5	38	10.76	8.46
09070390	128911	Filter Capt	2.5	11	0	0	****	****
12070390	128914	5 cm	140	110	137.5	99	32.78	30.04
11070390	128913	17 cm	210	190	207.5	179	37.75	35.99
10070390	128912	33 cm	190	220	187.5	209	48.31	46.50

TABLE A3-29

<u>Experimental Parameter:</u>	Promotor effect
<u>Sorbent:</u>	Marblehead AH Bag 7
<u>Promotor:</u>	Sodium Formate
<u>Promotor Conc:</u>	10 mol - % rel. to calcium
<u>Slurry Conc:</u>	20% wt-vol before promotor addition
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	H ₂
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
02080390	128904	Probe Capt	75	40	71.1	27	22.25	15.84
03080390	128915	Filter Capt	3.9	13	0	0	****	****
05080390	128917	17 cm	79	110	75.1	97	58.09	53.89
04080390	128916	33 cm	110	150	106.1	137	56.89	53.87

TABLE A3-30

<u>Experimental Parameter:</u>	Promotor effect
<u>Sorbent:</u>	Marblehead AH Bag 7
<u>Promotor:</u>	Sodium Acetate
<u>Promotor Conc:</u>	10 mol - % rel. to calcium
<u>Slurry Conc:</u>	20% wt-vol before promotor addition
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	H ₂
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent (%)	Ca util. corr. Percent (%)
02130390	128973	Probe Capt	13	13	11.1	5.3	41.72	19.92
03130390	128971	Filter Capt	1.9	7.7	0	0	****	****
06130390	128921	5 cm	200	110	198.1	102.3	22.95	21.54
05130390	128920	17 cm	210	270	208.1	262.3	53.64	52.59
04130390	128919	33 cm	520	660	518.1	652.3	52.95	52.53

TABLE A3-31

<u>Experimental Parameter:</u>	Promotor effect
<u>Sorbent:</u>	Marblehead AH Bag 7
<u>Promotor:</u>	Sodium Chloride
<u>Promotor Conc:</u>	10 mol - % rel. to calcium
<u>Slurry Conc:</u>	20% wt-vol before promotor addition
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	H ₂
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
02150390	128901	Probe Capt	300	110	298	102	15.30	14.28
03150390	128900	Filter Capt	2	8	0	0	*****	*****
06150390	128897	5 cm	180	160	178	152	37.08	35.63
05150390	128898	17 cm	480	590	478	582	51.28	50.80
04150390	128899	33 cm	330	490	328	482	61.95	61.31

TABLE A3-32

<u>Experimental Parameter:</u>	Promotor effect
<u>Sorbent:</u>	Marblehead AH Bag 7
<u>Promotor:</u>	Sodium Hydroxide
<u>Promotor Conc:</u>	10 mol - % rel. to calcium
<u>Slurry Conc:</u>	20% wt-vol before promotor addition
<u>SO₂ Conc:</u>	1500 ppm
<u>Fuel</u>	H ₂
<u>Rotor Speed:</u>	20 kRPM

Test No.	Sample No.	Sample ID	Ca mg/L	SO ₄ mg/L	Ca corr.	SO ₄ corr.	Ca util. meas. Percent	Ca util. corr. Percent
02160390	128894	Probe Capt	220	120	218.4	112.9	22.76	21.57
03160390	128895	Filter Capt	1.6	7.1	0	0	****	****
06160390	128892	5 cm	180	120	178.4	112.9	27.81	26.40
05160390	128891	17 cm	320	430	318.4	422.9	56.06	55.41
04160390	128896	33 cm	320	420	318.4	412.9	54.76	54.10

END

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02 / 08 / 91