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Presented at the
1987 AMERICAN INSTITUTE OF CHEMICAL ENGINEERS
SPRING NATIONAL MEETING
Houston, Texas
MARCH 29-APRIL 2, 1987

RST-67

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## ABSTRACT

The introduction of the Clean Air Act along with the continued development of fluidized bed combustion technology has combined to make the multi-solids fluidized bed combustor an excellent steam generator capable of utilizing low quality, high sulfur coals. Legislation limits the sulfur emission from a facility to 0.52 kg $SO_2$/GJ (1.2 lb $SO_2/10^6$ Btu). A theoretical model for the sulfur evolution and removal has been developed and calibrated with commercial data from a 14.7 MW ($50 \times 10^6$ Btu/hr) unit. The model and prediction are presented.

## INTRODUCTION

Circulating fluidized bed combustion processes have evolved from bubbling fluidized bed combustors during the past fifteen years. This evolution has come about to eliminate short comings such as poor carbon burnout and poor turndown characteristics in bubbling fluidized bed combustors. The Multi-Solids Fluidized Bed Combustor (MSFBC) is one circulating fluidized bed combustor which has commercially shown the minimization of burnout and turndown problems.

The MSFBC process is illustration Figure 1. It consists of an entrained bed of fine ash and limestone particles superimposed on a fluidized dense bed of large particles. The lower dense bed of large particles, which do not leave the combustor, serves to promote mixing and increase the residence time of the entrained ash, fuel, and limestone particles within the combustor. The combustor operates at superficial gas velocities of 7.5 to 10.5 m/s (25 to 35 ft/sec). An important feature of the MSFBC process is the essentially decoupled heat transfer and combustion processes. Most heat recovery occurs in an external heat exchanger (EHE) and a convective boiler. The EHE consists of heat exchanger tubes in a conventional fluidized bed operated at low velocities of 0.3 to 0.7 m/s (1 to 2 ft/sec). The combustor temperature is controlled to 1100 to 1200°K (1500 to 1700°F) by the recycling of entrained solids through the EHE.

A primary hot cyclone and non-mechanical ''L'' valves are used to separate and transport these solids. Flue gases leaving the cyclone separator are cooled in a conventional convective boiler. $NO_x$ control is achieved through staged combustion by operating the dense bed of the combustor under fuel rich conditions, and introducing secondary air in the entrained-bed region, or equivalent free board, to complete combustion. Since there are no heat exchange tubes immersed in the combustor dense bed, there is no danger of corrosion, or erosion. There are waterwalls in the upper combustor which remove approximately five to ten percent of the total energy.

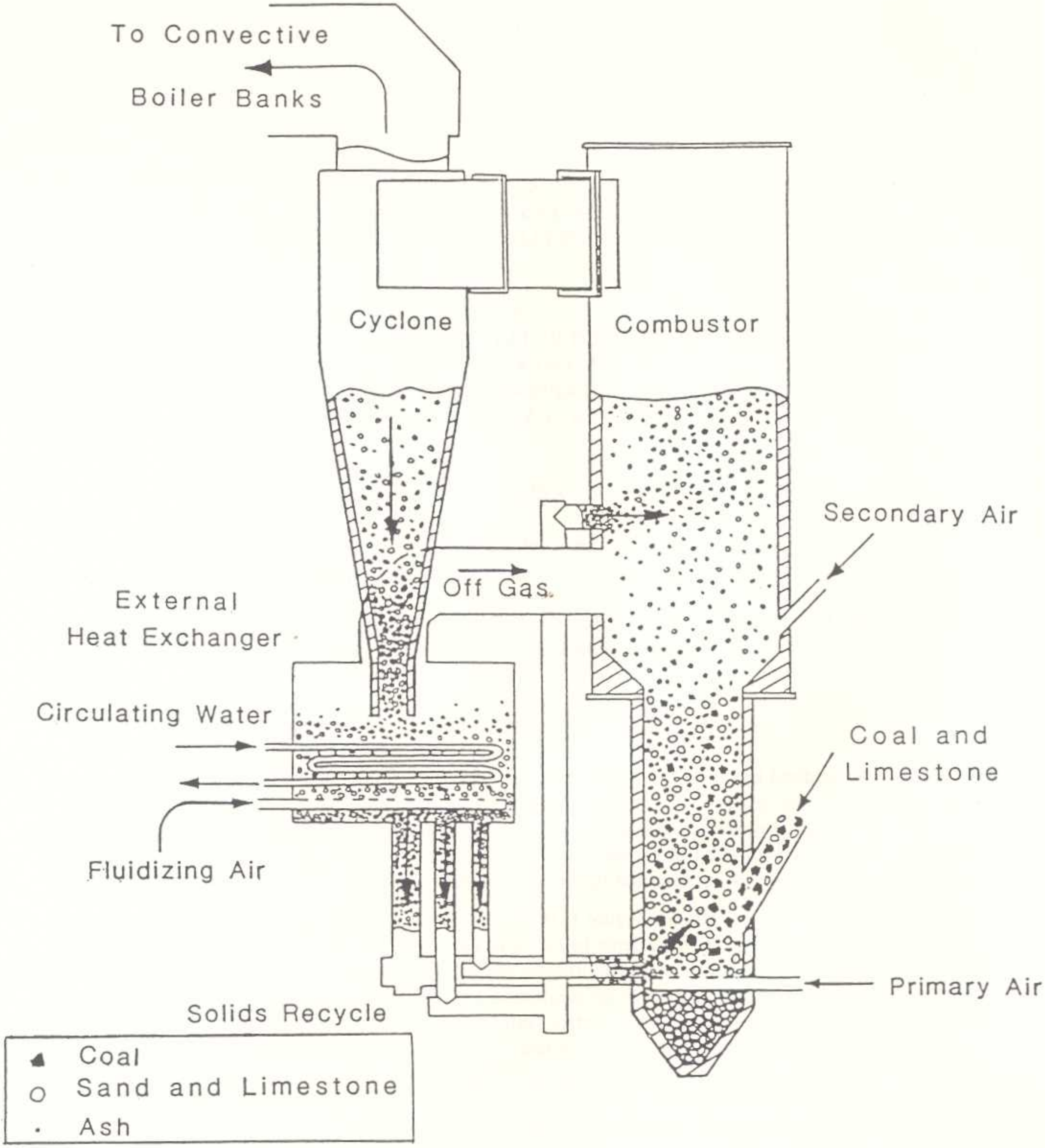


*Figure 1 MSFBC Process*

The sulfur removal model discussed in this paper includes detailed chemistry and fluid mechanics of the MSFBC process. Chemical reactions between the char and oxygen and between the sorbent, sulfur dioxide and oxygen are included. These reactions are discussed briefly in the background along with the fluid mechanics. Breault[1] provides grater details of the chemistry and fluid mechanics than covered in this paper.

## BACKGROUND

The MSFBC combustor dense bed and entrained bed exhibit two separate and distinct chemical and hydrodynamic environments. Both coal and limestone are fed to the dense bed. Devolatization and calcination occur in this region. The large particles of dense bed material promote fuel and limestone particle attrition to achieve smaller diameter transportable solids. The dense bed combustion products, both gaseous and particulate enter the entrained bed which is modeled by this work.

The devolatization process in the reducing zone produces a solid residue, char. The char is a composite material containing carbon, hydrogen, sulfur, oxygen, nitrogen and ash. An ultimate analysis of the char shows that the fractions of each of these elements are in approximately the same ratios as in the parent coal. Char oxidation is a heterogeneous chemical reaction which have been studied extensively[2]. The general heterogeneous chemical reaction is expressed as:

$$A_{gas} + bB_{solid} \xrightarrow{k} \text{products} \tag{1}$$

Written in this manner, the reactions for carbon, hydrogen and sulfur become:

$$O_2 + 2C \rightarrow 2CO \tag{2}$$

$$O_2 + C \rightarrow CO_2 \tag{3}$$

$$O_2 + 4H \rightarrow 2H_2O \tag{4}$$

$$O_2 + S \rightarrow SO_2 \tag{5}$$

This group of reactions is a simplification of possible reactions which have been researched and shown to exist in minor amounts[3]. The conversion of char components, specifically S, are required. This is necessary since $SO_2$ can not be removed unitl it has been generated. The rate of chemical conversion for the general reaction (1) with both bulk reactant diffusion and chemical kinetics controlling is given by:

$$R = \frac{dm_B}{dt} = \frac{A\ b\ M_B C_A}{\frac{1}{k_c} + \frac{1}{k_d}} \tag{6}$$

The two terms $\frac{1}{k_c}$ and $\frac{1}{k_d}$ are the chemical reaction resistance and the mass transfer resistance, respectively. The chemical reaction rate velocity (constant), $k_c$ has been studied extensively for the carbon-oxygen reaction[3,4]. However, reaction rate constants for the hydrogen-oxygen and sulfur-oxygen reactions are not available in published literature. The mass transfer coefficient, $k_d$ has been studied extensively for a single particle in a fluid and is obtained from the Sherwood Number.

The fluidized bed combustion of coal in a limestone bed has received considerable attention because of its ability to capture sulfur without requiring costly wet scrubbers. Sulfur removal in fluidized beds has been shown to be a function of the sorbent, the coal, and the system. Important process parameters for each of these major functional categories are listed in Table I. These parameters do not act independently of each other.

Measured $SO_2$ reductions as a function several process parameters are shown in Figure 2 for both bench and full scale MSFBC systems. As shown in Figure 2a, increased residence time, oxidizing plus reducing, results in higher sulfur removal. Larger particle size requires increased residence time for the same percent removal. Smaller particles are also more effective in reducing $SO_2$ emissions. Figure 2b shows the affect of the type of sorbent (dolomite versus limestone) on $SO_2$ control Calcium utilization is much higher for dolomite.

Calcium based dry sulfur removal processes involve the following chemical reactions;

$$CaCO_3 \rightarrow CaO + CO_2 \tag{7}$$

$$CaO + H_2S \rightarrow CaS + H_2O \tag{8}$$

$$CaS + 2O_2 \rightarrow CaSO_4 \tag{9}$$

$$CaO + SO_2 + 1/2\ O_2 \rightarrow CaSO_4 \tag{10}$$

Both the sulfination reactions (8 and 10) proceed forward at temperatures up to 1500°K (2250°F). However, the rate is only appreciable at temperatures between 1100 to 1225°K (1500 and 1750°F). Calcium oxide, CaO, is generated by the calcination of limestone ($CaCO_3$) or dolomite ($CaCO_3.MgCO_3$). Magnesium oxide (MgO) does not appear to sulfate at the temperatures existing in fluidized bed combustion. However, the formation of MgO does lead to improved calcium utilization through high stone porosity.

The reaction between hydrogen sulfide, and Calcium oxide occurs in the dense bed of the MSFBC. Renewed interest on limestone injection in low-$NO_x$ pulverized coal flames has generated recent investigations. The replacement of the carbon dioxide with the smaller calcium sulfide, CaS, molecule avoids the incomplete utilization of CaO due to the product layer formed by larger calcium sulfate molecules. The reaction rates for the two chemical reactions have been found to be of the same order of magnitude[5]. The reaction between CaO and $H_2S$ was actually found to be slightly faster. The MSFBC dense bed region makes use of this process to obtain calcium conversion in excess of the previously reported 60%.

**Table I**
**SULFUR REMOVAL DEPENDENCY**

**SORBENT***

- Stone type
  - limestone
  - dolomite
  - geological organization
- Calcination Environment
  - thermal
  - chemical
- Particle Size

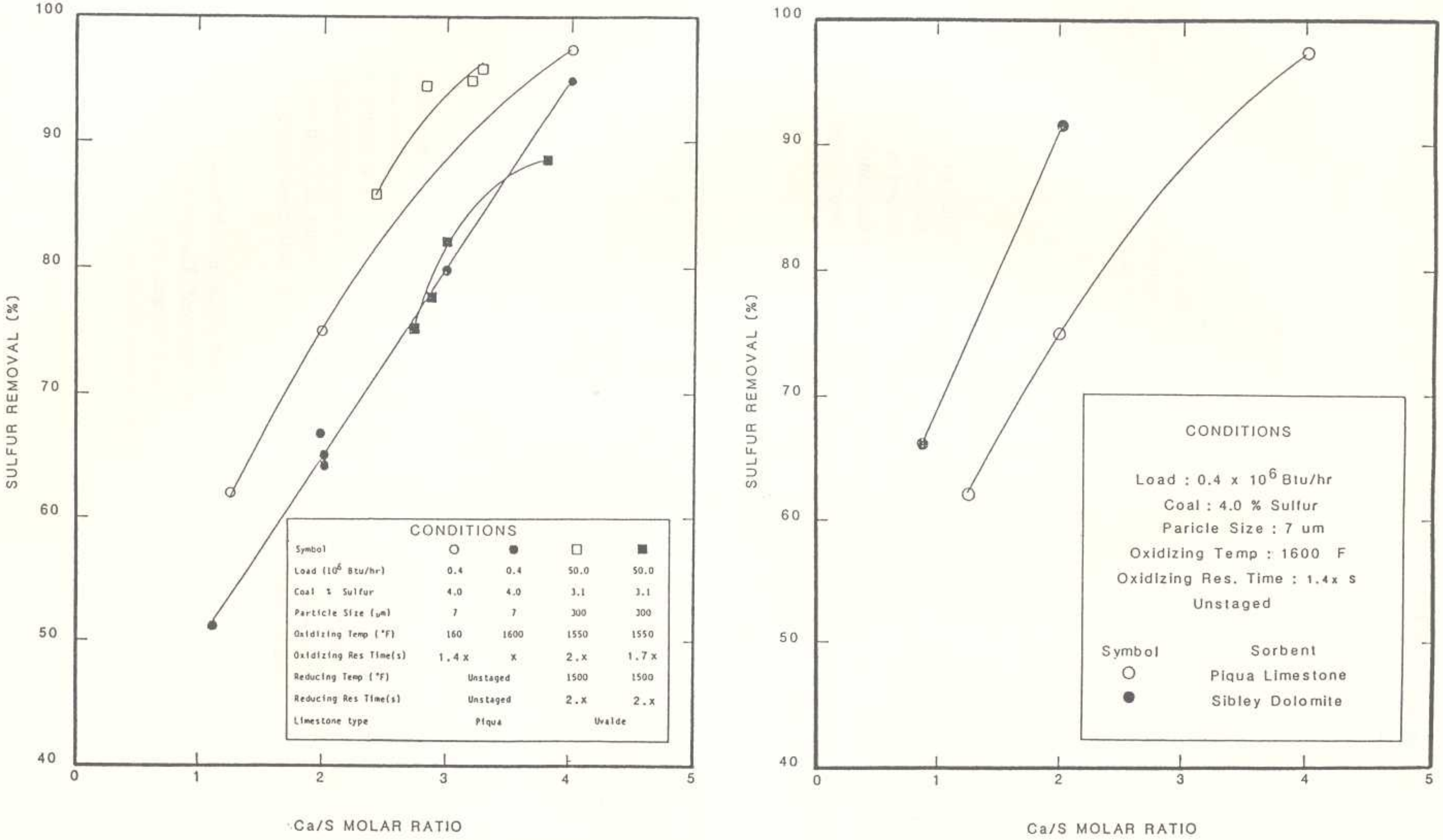
**COAL***

- Rank
- % Sulfur
- Particle Size

**SYSTEM***

- Temperature
- Solids Residence Time
- Gas Velocity
- Slip Velocity
- Void Fraction
- Coal Flow Rate
- Sorbent Flow Rate
- Chemical Environment

* These are not independent variables.



(a) Effect of Residence Time and Particle Size

(b) Effect ofStone Type

*Figure 2 MSFBC Sulfur Removal Data*

The rate for the reaction between $SO_2$ and CaO has been found to decay with time. This phenomenon is explained by the observation that pores are created in the stone structure by the calcination process. The actual decay in rate is attributed to the substitution of the much larger $SO_3$ molecule for the $CO_2$ molecule. This limits the conversion of calcium in limestones to approximately 60%. Two approaches have been taken towards modeling this phenomenon. Some have used a simple exponential decay model, while others have used complicated grain models. Grain models are more fundamental and probably more correctly describe the actual decay phenomenon. However, their complexity often limits their usefulness as an overall combustion process design model.

Borgwardt[6] has conducted extensive experimental studies on stone sulfination. By modifying the conventional Arrhenius frequency factor, he has modeled the reaction rate time decay phenomenon caused by pore plugging. Borgwardt described the reaction rate of a sorbent particle in a first order rate expression combining an initial frequency factor with an exponential decay function:

$$R \sim (A_o \, e^{-\beta m/w}) e^{-E/RT} C_{SO_2} \tag{11}$$

Kinetic parameters $A_o$, $\beta$, and E are obtained experimentally.

The MSFBC is a unique circulating fluidized bed process which consists of two fluidization regimes superimposed on each other. These are a dense turbulent bed and a lean entrained bed. The turbulent bed consist of large particles of an inert material utilized to reduce the fuel and sorbent particle sizes as well as increase the residence time of the solids in this zone. The entrained bed operates under oxidizing conditions to achieve efficient carbon burnout and sulfination product oxidation. Pneumatic transport theory is used to describe the hydrodynamics in this region. Details are provided elsewhere[1].

## MSFBC COMBUSTION MODEL

The coal combustion model for the MSFBC is discussed in two sections. The first section describes the coal oxidation model. It provides mass data for various species (i.e. Carbon and Hydrogen) in the coal at any height in the combustor. The respective species conversion rates is also generated. The second section describes the desulfurization model used to estimate the sulfur dioxide retained in the limestone/dolomite particles.

### *Char Oxidation*

The oxidizing zone of the combustor burns fine coal particles in the presence of calcium carbonate such that sulfur can be captured from the gaseous products in the reactor eliminating downstream clean up.

One of the objectives of this work has been to develop a model which would predict coal combustion efficiency and sulfur removal for the design of commercial MSFBC units. The assumptions used in the development of this model are summarized in Table II. The resultant process occurs as shown in Figure 3. A coal particle consisting of fixed carbon, hydrogen, sulfur and ash moves through the oxidizing zone at a velocity, $U_s$. The gas moves through the riser at a velocity, $U_g$. This results in a slip velocity $U_{sl}$, equal to the gas velocity less the solids velocity. The slip velocity controls the bulk mass transfer of oxygen or sulfur dioxide to the solid.

The model needs to address sulfur dioxide production, since the net sulfur dioxide remaining in the combustion products is the difference between that generated and that removed. The general differential equation shown earlier, Equation (6), is written for sulfur, carbon and hydrogen. These differential equations have been assembled in a computer model HVFBCC (High Velocity Fluidized Bed Coal Combustion)[1].

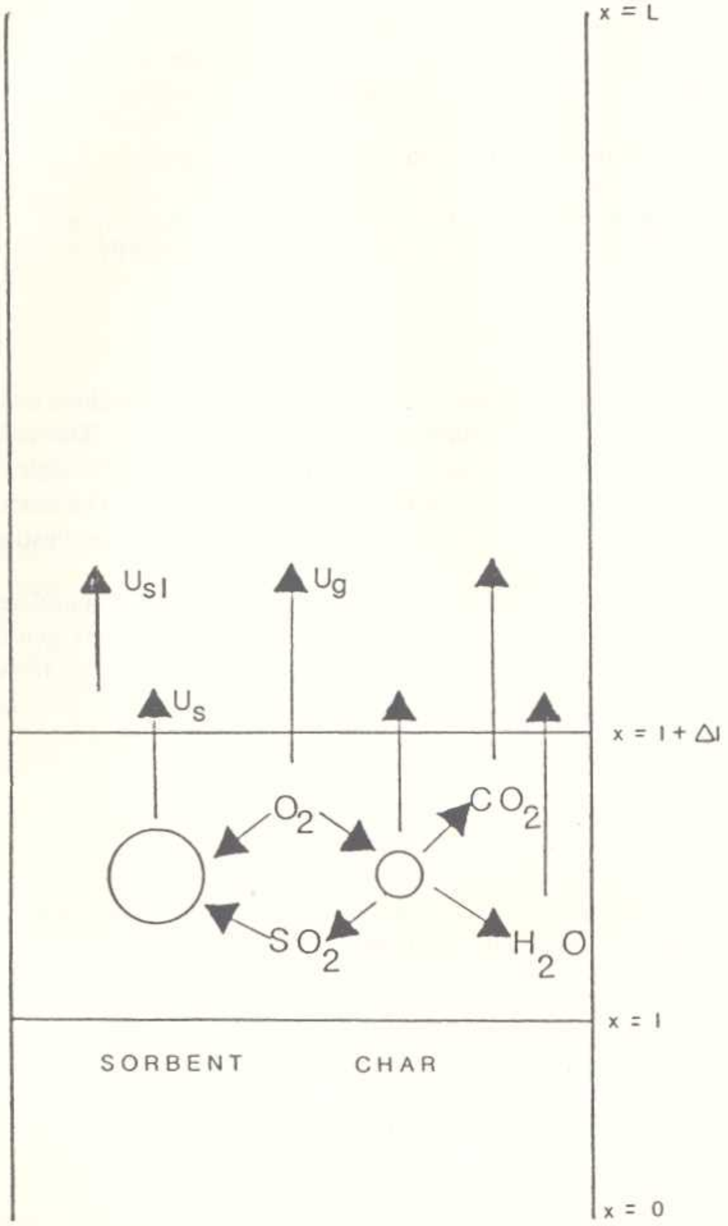


*Figure 3 Combustor Model Process Schematic*

## Table II
## OXIDIZING MODEL ASSUMPTIONS

1. Plug flow occurs.
2. Solid particles travel at velocity, $U_s$ and flux, $G_s$.
3. Gas flows at velocity, $U_g$ and flux, G.
4. The relative velocity between the solid and gas is $U_{sl}$.
5. The solids temperature is equal to the surrounding gas temperature.
6. Combustible volatile products are instantaneously oxidized into $H_2O$ and $CO_2$.
7. Nitrogen and oxygen volatile products, and moisture are released from the coal-char particle in the MSFBC dense bed.

*Flue Gas Desulfurization Model*

A fluidized bed, whether bubbling or high velocity can be used for its unique ability to remove sulfur dioxide from coal combustion products during the combustion process. The bubbling fluidized bed desulfurization process have been modeled extensively. On the other hand the high velocity fluidized bed desulfurization process like the MSFBC have only recently been modeled. The model for sulfur removal is developed using Equation 6 for sulfur dioxide production during coal combustion.

The coal desulfurization in the oxidizing plug flow zone of the MSFBC is considered to occur as shown in Figure 3. The combustion reactions which occur take place between the oxygen in the gas phase and the carbon, hydrogen, and sulfur in the coal. The desulfurization reaction occurs between the $O_2$, the product $SO_2$ and the CaO in the sorbent particle. The sulfur removed is dependent on the mass transfer, number of particles, and the kinetic rates. The net rate of $SO_2$ formation at any position is expressed by the relation:

$$\text{Net Formed} = \begin{array}{c}\text{Generated}\\ \text{by Combustion}\end{array} - \begin{array}{c}\text{Absorbed by}\\ \text{Sorbent particles}\end{array} \qquad (12)$$

The rate of sulfur oxidation for a single coal particle is multiplied by the number of coal particles in the cylindrical volume $\Pi d_t^2 \Delta L/4$ to obtain the total rate of $SO_2$ generated. This is expressed by the equation:

$$\frac{dm_{SO_{2,g}}}{dt} = -N_C \frac{M_{SO_2}}{M_S} \frac{dm_S}{dt} \qquad (13)$$

where $N_c$ is number of coal particles.

The total rate of $SO_2$ absorption is obtained by multiplying the absorption rate of one particle discussed earlier, corrected for external mass transfer, by the number of limestone particles, $N_S$. This is expressed by the equation:

$$\frac{dm_{SO_{2,a}}}{dt} = -\frac{N_S M_{SO_2} \pi d_p^2 C_{SO_2}}{\frac{1}{k_d} + \frac{1}{k_c}} \qquad (14)$$

The mass of sulfur dioxide in the gas is given from the equation (12) in mathematical terms:

$$\frac{dm_{SO_2}}{dt} = \frac{dm_{SO_{2,g}}}{dt} - \frac{dm_{SO_{2,a}}}{dt} \tag{12}$$

The model predicts the fraction of the total sulfur dioxide that is removed from the coal combustion process.

The sulfur dioxide emissions from the MSFBC are obtained by solving the six different equations, three for char oxidation and three for calcium sulfination. The fluid mechanics governing the mass transfer are supplied to the model as input along with the geometry.

## MODEL PREDICTION

In our process model of the MSFBC, the sulfination kinetics developed by Borgwardt are used to simulate the desulfurization process since it is both simple and accurate. The total rate of $SO_2$ absorption in the MSFBC is obtained by multiplying the absorption rate of one particle by the number of limestone particles in the volume under consideration.

This model has been applied to field data from a 14 MW ($50 \times 10^6$ Btu/hr) commercial MSFBC. As shown in Figure 4, the model accurately predicts the sulfur removal for the conditions given in the legend. The absolute average percent deviation between the model and data is 3.51%. Although additional modifications are required, the good agreement between the model and the data gives us confidence in the assumptions and in using this model to predict the performance of MSFBC combustor designs. The deviations between the predicted and experimental can be attributed to: (1) the accuracy of the kinetic data and (2) the accuracy of the flow field description, both input to the model.

## SUMMARY

A combustion/desulfurization chemical kinetic model has been used to predict the performance of the Multi-Solids Fluidized Bed Combustor. The MSFBC is described by a plug flow reactor model. The predictions from the model provide an estimate for the sulfur removal capabilities of a commercial scale MSFBC with an absolute average percent deviation of 3.51%. The model allows Riley to accurately predict MSFBC sulfur dioxide emissions. Future model work will include incorporating the fluid mechanics into the reactor kinetic model.

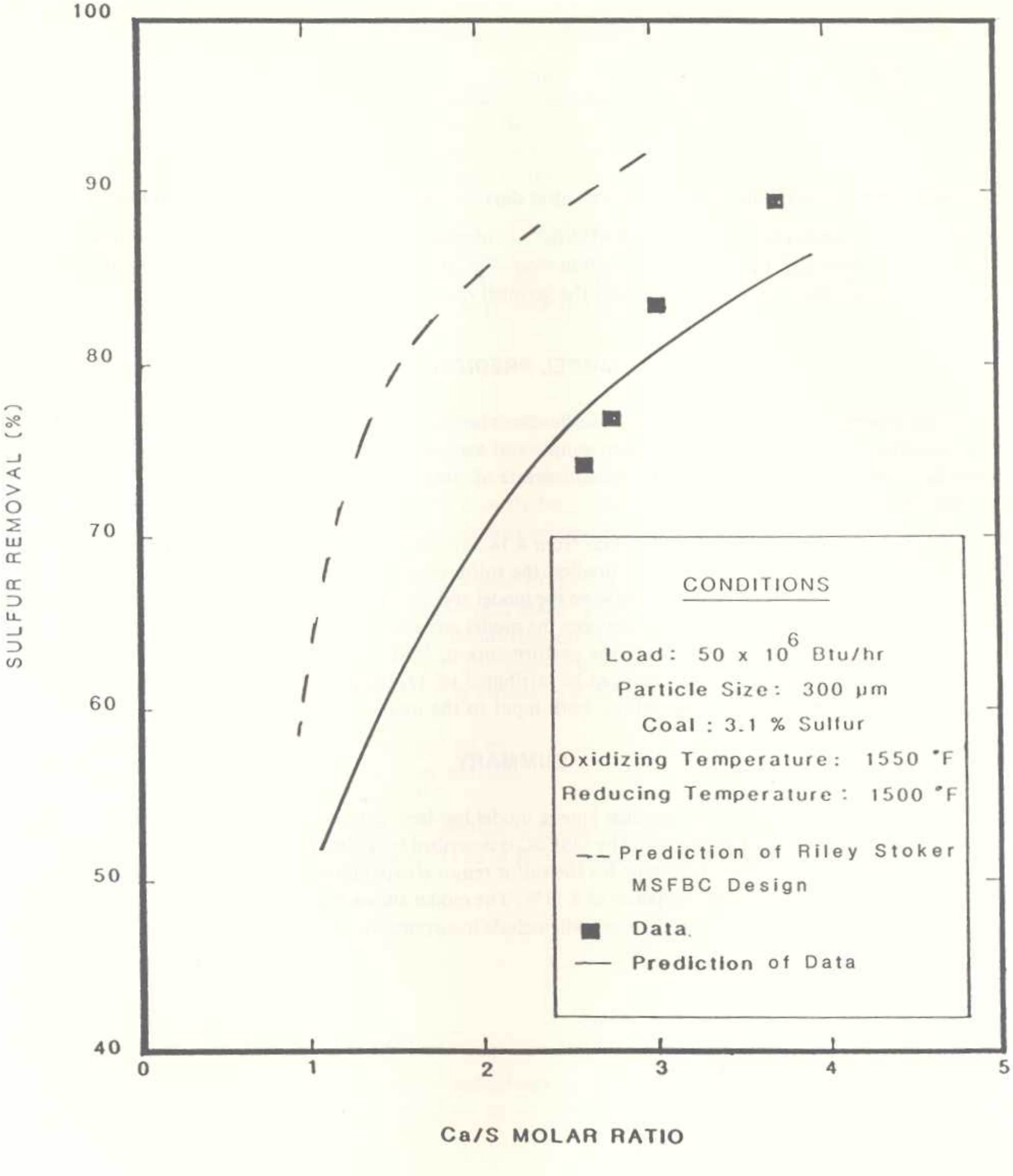


*Figure 4 Comparison of Model Prediction to Commercial Data*

## NOMENCLATURE

| | |
|---|---|
| $a$ | absorbed |
| $A$ | Surface are of particle |
| $A_o$ | Initial frequency factor |
| $b$ | Stoichiometric coefficient |
| $C$ | Concentration |
| $d_p$ | Particle diameter |
| $d_t$ | Combustor diameter |
| $D$ | Diffusivity |
| $E$ | Activation energy |
| $g$ | generated |
| $G$ | Gas Flux |
| $Gs$ | Solids flux |
| $k_c$ | Reaction rate velocity |
| $k_d$ | Mass transfer velocity |
| $\Delta L$ | Length of combustor element |
| $m$ | Mass |
| $M$ | Molecular weight |
| $N_C$ | Number of coal particles |
| $N_S$ | Number of sorbent particles |
| $R$ | Gas constant, sulfation rate |
| $t$ | Time |
| $Ug$ | Gas velocity |
| $Us$ | Solids velocity |
| $U_{s1}$ | Slip velocity |
| $w$ | Mass of limestone particle |
| $\beta$ | Sorbent activity loss coefficient |
| $1-\varepsilon$ | Solids volume factor |

## REFERENCES

1. Breault, Ronald, W., "Hydrodynamic Characteristics and Coal Combustion Modeling of a High Velocity Fluidized Bed" Ph.D. Thesis UNH, 1985.

2. Levenspiel, O., "Chemical Reaction Engineering", John Riley, NY, 1972.

3. Elliot, M. A., ed., "Chemistry of Coal Utilization—Second Supplementary volume", John Riley, NY, 1981.

4. Smoot, L. D., and Smith, P. J., "Combustion and Gasification of Coal, Char, and Coal/Water Mixtures", Course Notes, 1982.

5. Borgwardt, R. H., "Surface Area of Calcium Oxide and Kinetics of Calcium Sulfide Formation", Environmental Progress, Vol. 3, No. 2, 1984.

6. Borgwardt, R. H., "Kinetics of the Reaction of $SO_2$ with Calcined Limestone", Environmental Science and Technology, Vol. 4, No. 1, 1970.