THEORETICAL MODELING OF THE MULTI-SOLIDS FLUIDIZED BED COMBUSTOR: HYDRODYNAMICS, COMBUSTION, AND DESULFURIZATION

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ABSTRACT

The Multi-solids Fluidized Bed Combustor (MSFBC) is a unique high velocity circulating fluidized bed. The MSFBC is a process in which an entrained bed of fine ash and limestone particles is 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 oxidizing zone operates at superficial gas velocities of 25 to 35 ft/sec. The oxidizing zone of the MSFBC is a region of interest, since it is within this zone that combustion and desulfurization are completed.

This model extends the relative velocity, one dimensional, hydrodynamic two phase flow theory to include combustion and desulfurization chemical processes. The model is a one dimensional solution to the differential solids and gas continuity equations, the mixture momentum balance, the relative velocity model and the solids and gas energy balances. The model is calibrated with field data. Predictions are shown.

NOMENCLATURE

All units in SI.

a	Reaction order
A	Surface area of particle, frequency factor
A_o	Initial frequency factor
b	Stoichiometric coefficient, reaction order
C_D	Drag coefficient
C_{pi}	Specific heat of gas or solid
$\frac{d}{dx}$	Rate of change per unit length
de	Effective particle diameter
d_p	Particle diameter
d_{pi}	Particle diameter of species i
d_t	Combustor diameter

D	Diffusivity
E	Activation energy
fw	Wall friction
g	Gravity
G	Gas Flux
Gs	Solids flux
k_c	Reaction rate velocity
k_d	Mass transfer velocity
L	Length of combustor element
m	Mass
m	Mass flow rate
M	Molecular weight
R	Gas constant, sulfation rate
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number
t	Time
U_g	Gas velocity
U_s	Solids velocity
U_{s1}	Slip velocity
w	Mass of limestone particle
β	Sorbent activity loss coefficient
$1-\varepsilon$	Solids volume faction
ε	Gas volume fraction
γ	Fraction of particle area containing species i
ϱ_g	Gas density
ϱ_s	Solids density
$\bar{\varrho}_s$	Average solids density

INTRODUCTION

The MSFBC process, Figure 1, 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 25 to 35 ft/sec. An important feature of the MSFBC process is its 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 one to two ft/sec. The combustor temperature is controlled to 1500 to 1700°F by the recycling of entrained solids through the EHE.

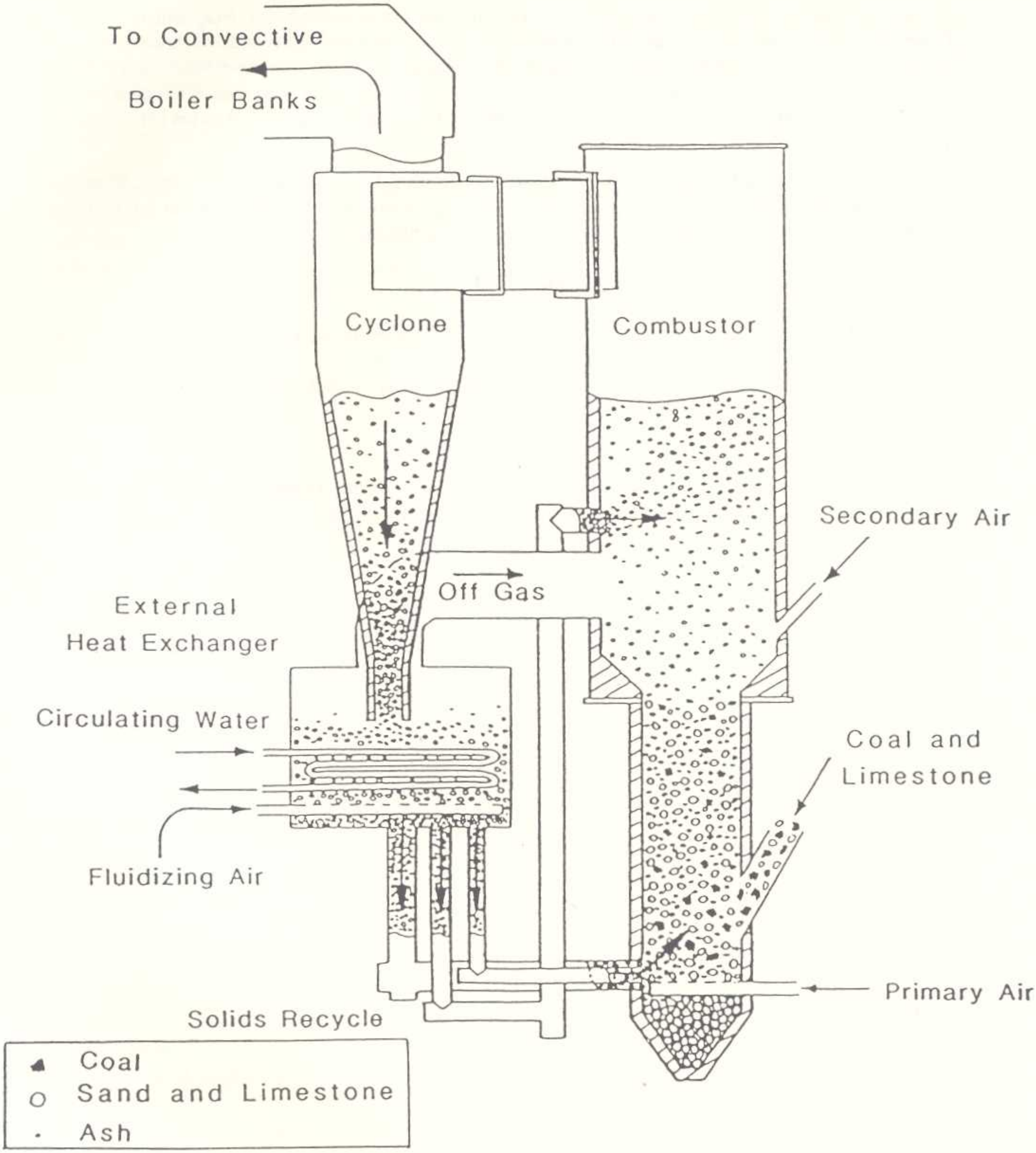


Figure 1 MSFBC Process

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.

The sulfur removal model discussed in this report includes detailed chemistry and fluid mechanics. Chemical reactions between the char and oxygen and between the sorbent, sulfur dioxide and oxygen are included. These reactions are discussed in the background along with the fluid mechanics.

BACKGROUND

The MSFBC oxidation zone is a vertical transport reactor designed to achieve efficient combustion and low emissions of SO_2 and NO_x. The theoretical model presented herein is an extension to the relative velocity fluid dynamic model developed by Gidispow[1] by including chemical reaction[2] and heat transfer.

Hydrodynamics

The relative velocity model which Gidispow[1] developed through minimizing the entropy field from a non-equilibrium formulation is summarized by the following equations: the gas continuity equation

$$\frac{d}{dx} (\varepsilon \varrho_g U_g) = 0 \tag{1}$$

the solids continuity equation

$$\frac{d}{dx} [(1-\varepsilon) \varrho_s U_s] = 0 \tag{2}$$

the mixture momentum equation

$$\begin{aligned} &(1-\varepsilon) \varrho_s U_s \frac{dU_s}{dx} + \varepsilon \varrho_g U_g \frac{dU_g}{dx} + \\ &g [\varrho_s (1-\varepsilon) + \varrho_g \varepsilon] = - \frac{dP}{dx} - fw \end{aligned} \tag{3}$$

and, the relative velocity equation

$$U_{sl} \frac{dU_g}{dx} - U_{sl} \frac{dU_s}{dx} + \frac{3}{4} C_D \frac{\varrho_g}{\varrho_s} \frac{U_{sl}2}{d_e} \varepsilon - 2.65 = g \tag{4}$$

The wall friction is represented by the term fw, while the gas-solids drag is obtained from the drag coefficient for a single particle adjusted for multiple particles by the method of Richardson and Zaki.

Combustion Kinetics

The reaction kinetics in fluidized bed combustor are complex heterogeneous processes involving coal, sorbent and gas species. Detailed chemistry of these processes can be found elsewhere [2,3,4,5]. A brief summary is provided below.

Char Oxidation

The devolitization process in the reducing zone produces a solid residue, char. The char consists of the fixed carbon and ash. In actuality, 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 s a heterogeneous chemical reaction. The general heterogeneous chemical reaction is expressed as:

$$A_{gas} + bB_{solid} \xrightarrow{k} \text{products} \tag{5}$$

The rate of chemical reaction for the general first order reaction with bulk mass transfer and chemical kinetics controlling is given by:

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

The two terms $\frac{1}{k_c}$ and $\frac{1}{k_d}$ are the chemical reaction resistance and the mass transfer resistance, respectively.

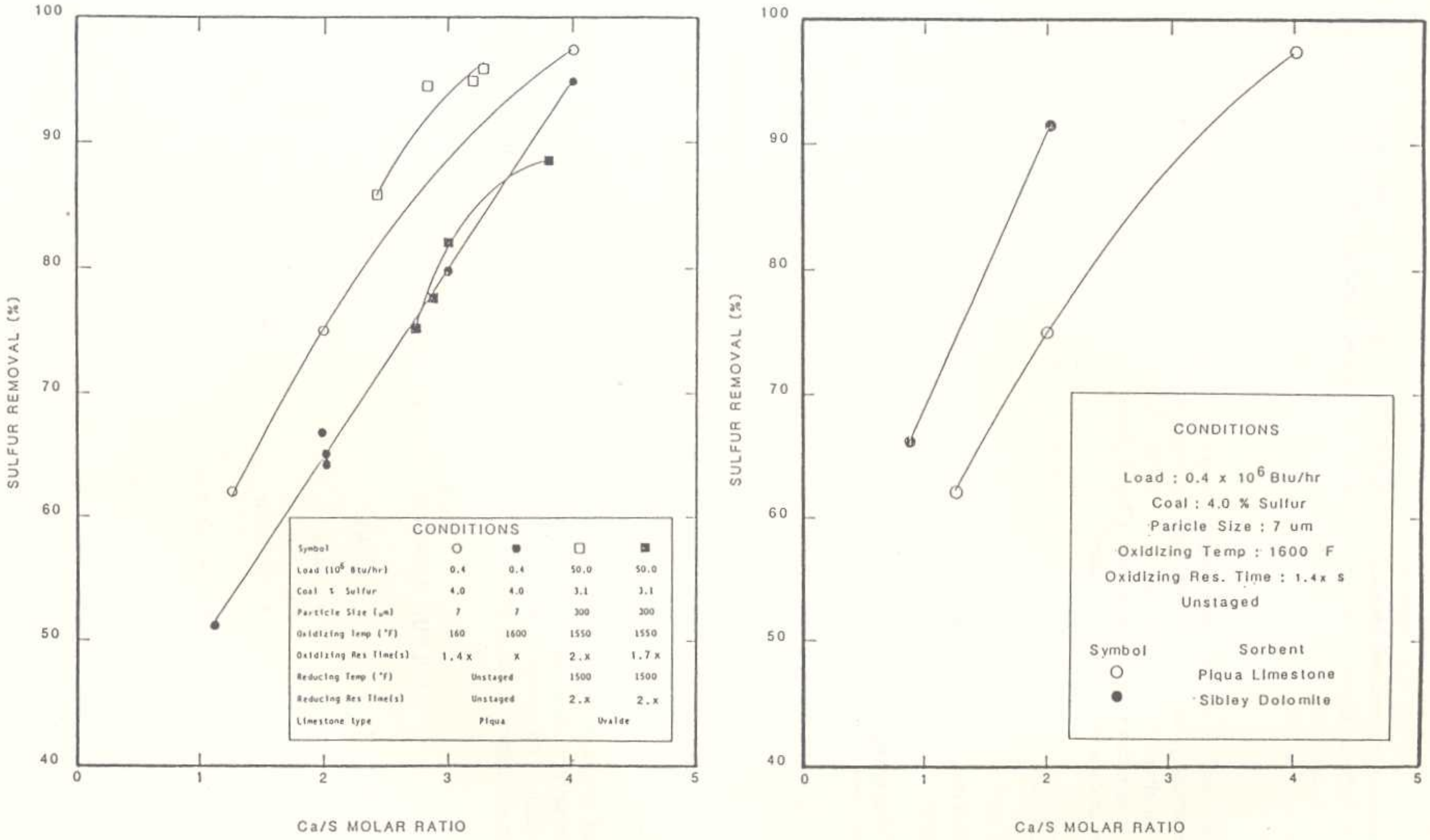
SO_2 Removal

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.

Table I
SULFUR REMOVAL DEPENDENCY

SORBENT *	COAL *	SYSTEM *
• Stone type - limestone - dolomite - geological origination • Calcination Environment - thermal - chemical • Particle Size	• Rank • % Sulfur • Particle Size	• 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

TABLE II
OXIDIZING ZONE CHEMICAL REACTIONS

Reaction Number	Reaction
1	$2CO + O_2 \rightarrow 2CO_2$
2	$NO + CO \rightarrow 2\ N_2 + CO_2$
3	$O_2 + 2C_{(s)} \rightarrow 2CO$
4	$O_2 + 4H_{(s)} \rightarrow 2H_2O$
5	$O_2 + S_{(s)} \rightarrow SO_2$
6	$O_2 + 2N_{(s)} \rightarrow 2NO$
7	$O_2 + 2\ O_{(s)} \rightarrow 2O_2$
8	$SO_2 + CaO_{(s)} \rightarrow CaSO_{3(s)}$
9	$O_2 + 2CaSO_{3(s)} \rightarrow 2\ CaSO_{4(s)}$
10	$NO + C_{(s)} \rightarrow \frac{1}{2}\ N_2 + CO$
11	$NO + CaSO_{3(s)} \rightarrow \frac{1}{2}\ N_2 + CaSO_{4(s)}$
12	$SO_2 + \frac{1}{2}\ O_2 + CaO_{(s)} \rightarrow CaSO_{4(s)}$

The overall continuity equation for the gas and solids are given by:

$$\frac{d}{dx}(\varepsilon \varrho_g U_g) = S_g \tag{13}$$

$$\frac{d}{dx}[(1-\varepsilon)\ \varrho_s\ U_s] = S_s \tag{14}$$

where S_g and S_s are the gaseous and solids generation terms. The mixture momentum equation for vertical gas-solids transport and the relative velocity model have been developed based on minimizing entropy production by Gidispow. These are equations (3) and (4).

In addition to the overall continuity equations, component equations are required. These equations take the form:

$$\frac{d}{dx}[\varepsilon \varrho_{gi}\ U_g] - S_{gi} = 0 \tag{15}$$

for the gas and

$$\frac{d}{dx}[(1-\varepsilon)\ \varrho_{si}\ U_s] - S_{si} = 0 \tag{16}$$

Measured SO_2 reductions as a function of several process parameters are shown in Figure 2 for both bench and full scale systems. As shown in Figure 2a, increased gas 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. The dense bed in the MSFBC promotes the breakdown of larger particles to smaller particles, which are entrained and contact the sulfur làden SULFUR REMOVAL DEPENDENCY flue gas. Figure 2b shows the affect of the type of sorbent (dolomite versus limestone) on SO_2 control. Calcium utilization is much higher for dolomite.

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 effectively sealing off the stone core. 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[5] has conducted extensive experimental studies on stone sulfation. 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:

$$R \sim (A_o \, e^{-\beta m/w}) \, e^{-E/RT} C_{SO_2} \tag{12}$$

Kinetic parameters A_o, β, and E are obtained experimentally.

TRANSPORT COMBUSTION—DESULFURIZATION MODEL

The Multi-solids Fluidized Bed Combustor (MSFBC) consists of two hydrodynamic regimes superimposed on one-another. These two regimes are: (1) a turbulent fluidized bed and (2) a transport bed. The model developed in this paper concerns the transport bed only. The computer code COMSUL describes the COMbustion and deSULfurization in the transport bed. It assumes the properties and reaction products leaving the turbulent bed as input to the transport bed calculations. The application of these assumptions reduces the number of chemical species the transport model needs to track to the following: CaO, $CaSO_4$, CO_2, Char-C, H, S, N and O, Stone ash, coal ash, solid inerts, N_2, O_2, CO, H_2O, NO, and SO_2. The consumption and production of these species occur through the 12 reactions presented in Table II.

The transport model considers the material contained in the control volume shown in Figure 3 and flow rates into and out of the volume in the solution of the continuity, momentum, and energy balances. Figure 3 shows the flow rate of char, sorbent, inert solids, and gas.

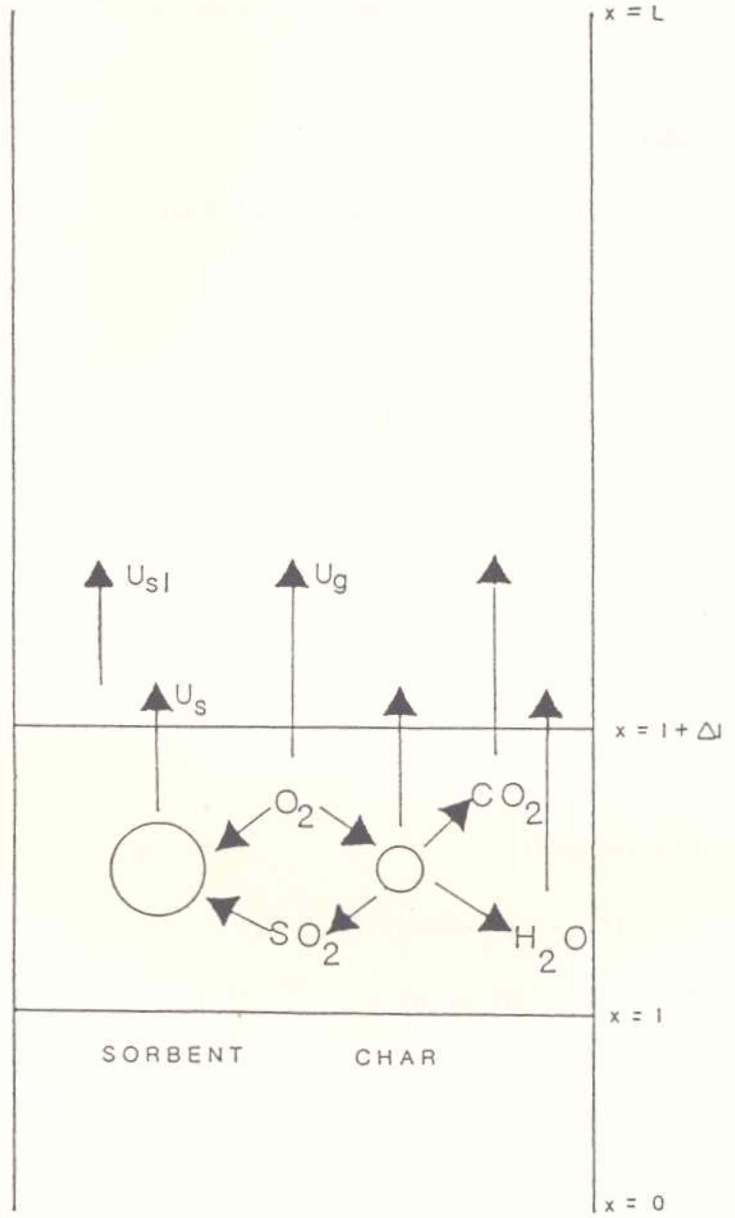


Figure 3 Combustor Model Process Schematic

for the solids. The rate of generation of either the solids or gas, S_i is the sum of the contribution from the 12 reactions listed in Table I which involved species i. For example, the rate of production of CO involves reactions 1, 2, 3, and 10 and is given by the expression:

$$S_{CO} = R_1 + R_2 - R_3 - R_{10} \tag{17}$$

The homogeneous rates for reactions 1 and 2 are given by the expressions:

$$R_1 = k_1[CO]\,[O_2]^a\,[H_2O]^b, \tag{18}$$

$$R_2 = k_2[CO]\,[NO]^a\,[H_2O]^b, \tag{19}$$

respectively. The rates for the heterogeneous reactions 3 and 10 are:

$$R_3 = \frac{6(1\text{-}\varepsilon)_c(2)\,[O_2]\,\gamma_c}{(\pi\, d_{pc})\left(\dfrac{1}{k_3} + \dfrac{1}{k_{d,O_2}}\right)} \tag{20}$$

and

$$R_{10} = \frac{6(1\text{-}\varepsilon)_c\,(1)\,[NO]\,\gamma_c}{(\pi\, d_{pc})\left(\dfrac{1}{k_{10}} + \dfrac{1}{k_{d,NO}}\right)} \tag{21}$$

The energy equation for the gas is:

$$\begin{aligned} \dot{m}_g\, Cp \frac{d}{dx}(T_g) = {} & -hp\,\alpha\,(T_g - T_s) - U(\pi dt)\,(T_g - T_w) \\ & + \left(\frac{d\dot{m}_{CHAR}}{dx}\right)(-\Delta H_{CHAR}) + \left(\frac{d\dot{m}_{CO}}{dx}\right)(-\Delta H_{CO}) \\ & + \left(\frac{d\dot{m}_{NO}}{dx}\right)(-\Delta H_{NO}) - C_{pg}\left(\frac{d\dot{m}_g}{dx}\right) T_g \end{aligned} \tag{22}$$

and for the solid is:

$$\begin{aligned} \dot{m}_s\, C_{ps} \frac{d}{dx}(T_s) = {} & -\left(\frac{d\dot{m}_{CaSO_4}}{dx}\right)(-\Delta H_{CaSO_4}) + \\ & hp\,\alpha\,(T_g - T_s) - C_{ps}\left(\frac{d\dot{m}_s}{dx}\right) T_s \end{aligned} \tag{23}$$

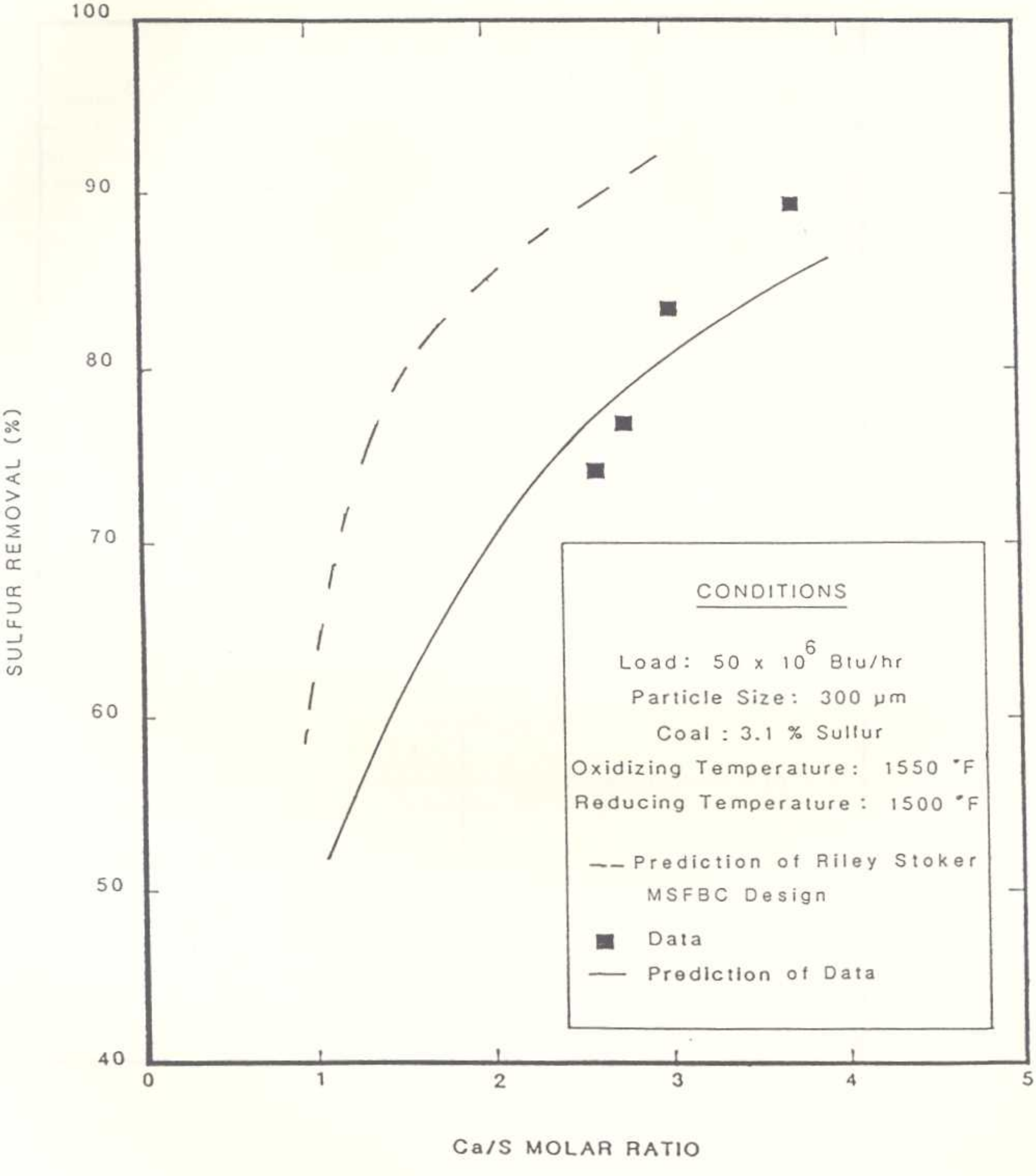


Figure 4 Comparison of Model Prediction to Chemical Data

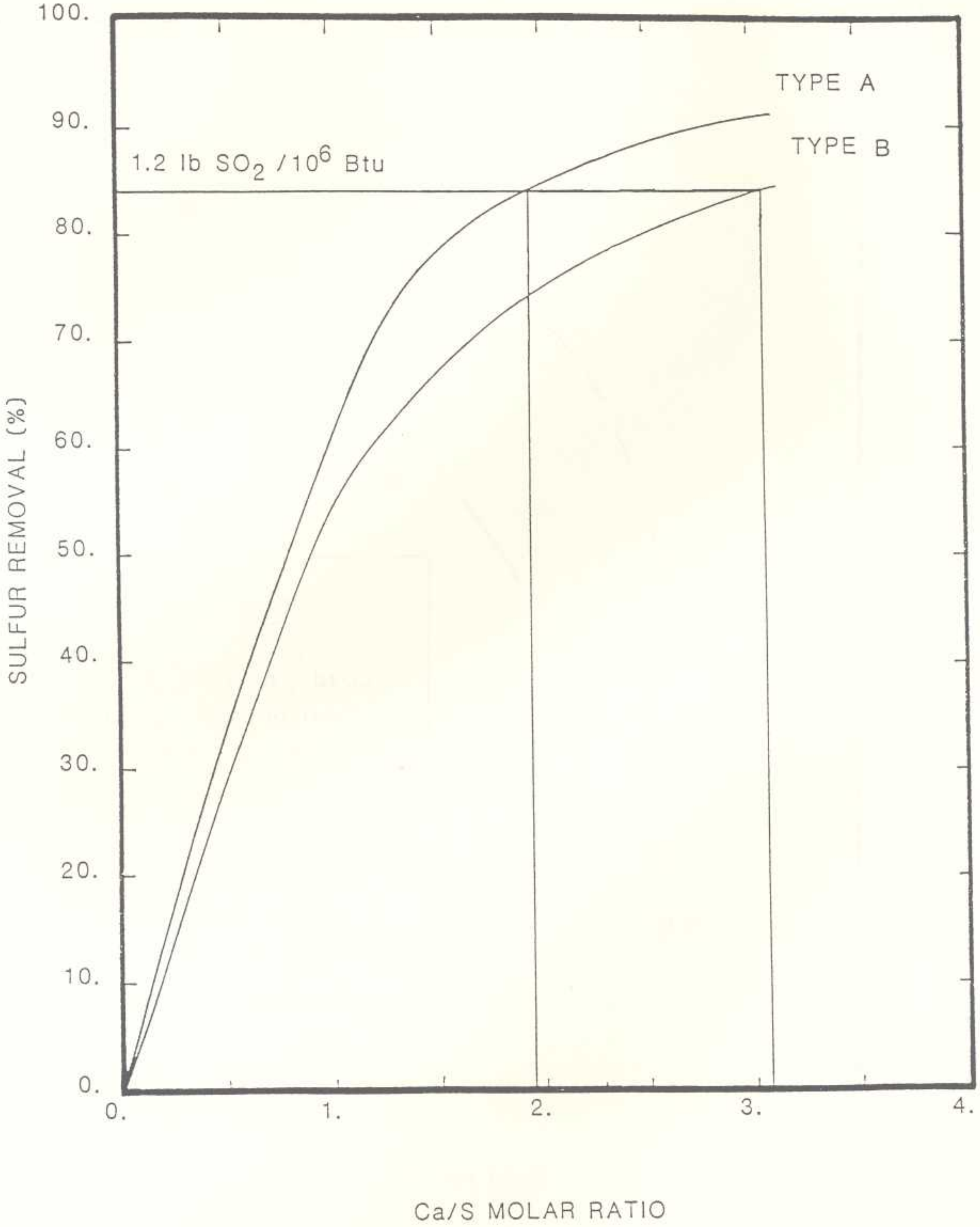


Figure 5 Sulfur Predictions for Two Limestone Types

The gas generation term $\frac{dm^{\cdot}_g}{dx}$ is obtained by summing the contribution to the gas molar flow rate from each of the reactions presented in Table II. The solids generation term $\frac{dm^{\cdot}_s}{dx}$ is obtained similarly.

MODEL PREDICTION

The results of a computer reactor model are only believable when checked against real conditions. This model has been compared to field data from a 14 MW (50 × 10^6 Btu/hr) commercial MSFBC. As shown in Figure 4, the model accurately predicts the sulfur removal for the conditions given in the table. 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 using this model to predict the performance of MSFBC combustor designs. The deviations between the predicted and experimental can be attributed to the accuracy of the kinetic and field data. Figure 4 also contains the sulfur removal prediction of a MSFBC designed to have 85% sulfur removal using a Ca/S ratio of 2.0. This curve is labled optimumly designed MSFBC.

The usefulness of this code is demonstrated by the comparison of two limestones presented in Figure 5. It is seen for the same unit, that one limestone requires a 50% increase in its feedrate over the other limestone to achieve the same sulfur removal. With the ability to predict sulfur removal efficiencies for various limestone feed stocks, the MSFBC is designed to provide the most economical sulfur removal.

SUMMARY

A combustion/desulfurization chemical kinetic and transport 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 3.5%. The model allows Riley to accurately predict MSFBC sulfur dioxide emissions.

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