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Spectral Methods Applied to Fluidized Bed Combustors **OSTI**

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NOMENCLATURE

Roman letters

a	absorptivity
a	coefficient in devolatilization rate power law (s)
A	devolatilization coefficient in coal combustion model $= Q\{[CO_2]_i - [CO_2]_f\} = Ng_o$
A	infrared absorbance
A	matrix of absorbances
A	pre-exponential factor in Arrhenius law (1/s)
A_a	pre-exponential factor in Arrhenius law (1/s) applied to chemical rate coefficient
A_b	bed area (m ²)
a_{cc}	surface area of unreacted CaCO ₃ core (m ²)
a_{gc}	surface area of unreacted CaO grain core (m ²)
A_i	pre-exponential factor for devolatilization of individual pseudo-species (1/s)
a_o	factor in char burnout rate constant power law (m/s)
A_p	particle external surface area (m ³)
a_p	surface area of particle (m ²)
a_{sc}	surface area of unreacted CaO particle core (m ²)
B	char coefficient in coal combustion model $= [CO_2]_f [CO_2]_s = \frac{N\pi\rho_c d_i}{2\tau_c}$
b	pathlength of FTIR gas cell (m)
b	slope
c	concentration
C	concentration matrix
c_{1c}	constant #1 for calcination $= \{[CO_2]_E - [CO_2]_I\} M_{CaCO_3} / f_{CaCO_3} P_{LS}$

c_{1s}	constant #1 for sulfation = $[\text{SO}_2]_i M_{\text{CaO}} / f_{\text{CaCO}_3} p_{\text{CaO}}$
c_2	constant #2 = $S m / \rho_{\text{LS}} Q$
C_A	concentration of species A (mol/m^3)
C_{Ag}	concentration of species A in reactor (mol/m^3)
C_{Ao}	initial concentration of species A (mol/m^3)
c_m	mass fraction of initial coal to be reacted
C_p	oxygen concentration in particulate phase (mol/m^3)
$[\text{CO}_2]$	CO_2 concentration as a function of radial position in the particle (mol/m^3)
$[\text{CO}_2]_A$	concentration of CO_2 at analyzer (mol/m^3)
$[\text{CO}_2]_{\text{avg}}$	average concentration of CO_2 in the combustor steady state background emissions (mol/m^3)
$[\text{CO}_2]_E$	equilibrium CO_2 concentration for reversible Eqn. (2.1)
$[\text{CO}_2]_f$	$N(g_o + k d_i^2 [\text{O}_2]_e) / Q$ (mole/m^3)
$[\text{CO}_2]_i$	CO_2 concentration at inlet (mol/m^3)
$[\text{CO}_2]_j$	$N k d_i^2 [\text{O}_2]_e / Q$ for char coal combustion (mol/m^3)
$[\text{CO}_2]_o$	initial concentration of CO_2 in bed (mol/m^3)
$[\text{CO}_2]_R$	concentration of CO_2 exiting the reactor (mol/m^3)
$[\text{CO}_2]_s$	CO_2 concentration at particle surface (mol/m^3)
d	coal particle diameter (mm)
D	effective coefficient of molecular diffusion of oxygen in the flue gas
D_a	general bulk diffusion coefficient of species a (m^2/s)
D_{AB}	binary diffusion coefficient of A in B (m^2/s)
D_b	bed diameter (m)
D_e	intraparticle diffusion coefficient (m^2/s)
D_{ec}	effective diffusivity of CO_2 in particle pores (m^2/s)

D_{es}	effective diffusivity of SO_2 (m^2/s)
D_{eso}	initial effective diffusivity of SO_2 (m^2/s)
d_f	diameter of spherical fragment following primary fragmentation (mm)
D_G	molecular diffusion coefficient in gas phase
ΔH	standard enthalpy of formation ($kJ/kg^\circ C$)
ΔH	heat of reaction (kcal/mol)
d_i	initial coal particle diameter (mm)
D_m	diffusivity of oxygen to the coal particle (m^2/s)
d_p	particle diameter, (m)
D_{pl}	product layer diffusivity (m^2/s)
E	activation energy (cal/mol)
E_a	activation energy
E_a	apparent activation energy for the combustion of char (cal/mol)
E_i	activation energy for volatiles release for individual species i (cal/mol)
E_o	mean activation energy (cal/mol)
E_v	overall activation energy for volatiles release (cal/mol)
f_{CaCO_3}	mass fraction of $CaCO_3$ in limestone
f_{CaO}	mass fraction of CaO in limestone
$\mathfrak{F}$	Fourier transform operator
$g(t)$	dynamic system transfer function
g_o	rate of production of CO_2 from combustion of volatiles (mol/s/particle)
h	a convective heat transfer coefficient
H	fluidized bed height (m)
h_c	film mass transfer coefficient for CO_2 diffusion (m/s)

h_m	mass flux of oxygen per unit area of surface per unit of concentration difference
h_T	film heat transfer coefficient ($\text{kcal/m}^2\cdot\text{K}$)
I_B	intensity of the infrared energy without the sample in place
I_s	infrared energy through a sample
K	absorptivity matrix,
K	dimensionless reaction rate coefficient = $k_s S_o/Q$
K	dynamic system gain
k	overall char reaction rate constant (m/s)
k^*	reaction rate coefficient for carbonation reaction ($\text{mol/N}\cdot\text{m}\cdot\text{s}$)
k_1	rate constant for first parallel reaction ($1/\text{s}$)
k_2	rate constant for second parallel reaction ($1/\text{s}$)
k_c	calcination reaction rate coefficient ($\text{m}^3/\text{mol}\cdot\text{s}$)
k_c	overall mass transfer coefficient for the reactive volatiles
k_c^*	thermal conductivity of CaO ($\text{kcal/m}^2\cdot\text{K}$)
k_d	diffusion rate of gas to particle surface ($\text{kg(C)}/(\text{m}^2 \text{ kPa s})$)
k_d	diffusivity decay rate constant (s^{-1})
k_g	gas thermal conductivity
k_i	volatiles pseudo-species rate constant ($1/\text{s}$)
k_o	surface reaction rate constant for char burnout (m/s)
k_s	sulfation reaction rate coefficient (m/s)
k_v	general intrinsic reaction rate constant ($1/\text{s}$)
k_v	volatiles release rate constant ($1/\text{s}$)
k_v	volumetric reaction rate ($\text{m}^3/\text{mol}\cdot\text{s}$)
L	bed depth (m)
L	dimensionless length (m) = $t/2$ for flat plates, r for cylinders and spheres

m	constant heating rate (deg/s) used in devolatilization rate equation
m	mass of carbon in particle or batch (g, kg)
M	molecular weight of diffusing species (g/mol)
m_c	cumulative carbon reacted during batch test (g, kg)
M_c	molecular weight of carbon (g/mol)
M_{CaCO_3}	molecular weight of $CaCO_3$ (g/mol)
m_{coal}	mass of coal batched in the fluidized bed (g)
m_i	initial mass of carbon in char particle (g)
M_L	molecular weight of limestone (g/mol)
m_{LS}	mass of limestone batch (g)
m_t	total amount of carbon in batch dump (g, kg)
n	apparent reaction order
n	exponent in char burnout time power law
n	oxygen transfer rate to one particle
$n(t)$	white noise input function
$n_{1,2}$	number of data points on regression line
N	number of coal particles in bed
$\dot{N}$	molar flow of oxygen to a single coal particle (mol/s)
N_f	number of spherical fragments following primary fragmentation
N_p	number of particles per limestone batch
n_p	number of particles per limestone batch
$[O_2]_e$	oxygen concentration in emulsion phase of fluidized bed (mol/m ³)
$[O_2]_i$	oxygen concentration at fluidized bed inlet (mol/m ³)
P	total pressure (Atm)
p_E	equilibrium partial pressure for calcination/carbonation reaction (Atm)

p_g	partial pressure of oxygen in the bulk gas
p_R	instantaneous partial pressure of CO_2 (Atm)
Pr	Prandtl number
p_s	partial pressure of oxygen on the coal particle surface
q	mass of carbon oxidized per unit area of particle outer surface per second, ($\text{kg}/\text{m}^2\text{s}$),
Q	volumetric flow rate through the combustor (m^3/s)
Q	heat generation rate in fluidized bed combustion
Q_b	total gas exchange rate from each bubble
r_{cc}	radius of unreacted CaCO_3 core (m)
r_p	particle radius (m)
r_{sc}	radius of unreacted CaO core (m)
R	universal gas constant, $8.314 \text{ kJ}/(\text{kg K})$, $1.9872 \text{ cal}/\text{deg mole}$
Re	Reynolds number $= U d_p / \mu$
Re_p	particle Reynolds number $= U_o d_p / \nu$
$R_{\text{chemical reaction}}$	resistance to reaction due to chemical reaction
$R_{\text{film diffusion}}$	resistance to reaction due to film diffusion
$R_{\text{pore diffusion}}$	resistance to reaction due to pore diffusion
R_{yy}	autocorrelation function
S	external surface area of particles in the batch (m^2)
S	shape factor = 1 for flat plates, 2 for cylinders, 3 for spheres
S_{bd}	standard deviation for the difference of the slopes
Sc	Schmidt number $= \mu / \rho D_g = \nu / D$
Sc	Schmidt number $= \nu / D$
S_g	material specific surface area (m^2/g)

Sh	Sherwood number = $hd_p/\mathcal{D}$
S_o	initial external surface area of particles in the batch (m^2)
S_{xx}	power spectral density of output function
S_{yx}	standard error of y on x
S_{ypc}	combined standard error of y on x for two slopes
S_{yy}	power spectral density of input function
$[SO_2]_{gc}$	SO_2 concentration at the CaO grain core (mol/m^3)
$[SO_2]_i$	combustor inlet SO_2 concentration (mol/m^3)
$[SO_2]_o$	initial SO_2 concentration in the reactor (mol/m^3)
$[SO_2]_R$	SO_2 concentration in and leaving the combustor (mol/m^3)
$[SO_2]_s$	SO_2 concentration at the particle surface (mol/m^3)
$[SO_2]_{sc}$	SO_2 concentration at the particle CaO core surface (mol/m^3)
T	infrared energy transmittance in an FTIR
t	reaction time (s)
t	t statistic
T	temperature (K)
t	time (s)
T_b	bed temperature (K)
t_b	char burnout time (s)
T_{bed}	bed temperature (K)
t_c	char burnout time, chemical kinetics control (s)
t_c	time to complete calcination (s)
t_d	char burnout time, diffusion control (s)
T_f	characteristic frequency of dynamic system
T_m	boundary layer temperature (K)

t_o	initial time associated with the instrument lag response (s)
T_p	particle temperature (K)
t_{pl}	product layer thickness (m)
t_v	total devolatilization time (s)
u	superficial bed velocity (m/s)
$u(t)$	input function to a dynamic function
u_a	bubble velocity (m/s)
U_o	bed superficial velocity (m/s)
u_o	minimum fluidization velocity (m/s)
v	devolatilization power law exponent
V	fraction of volatiles released from coal particles
$V_{\infty,1}$	fraction of volatiles released from coal particles for first parallel reaction
$V_{\infty,2}$	fraction of volatiles released from coal particles for second parallel reaction
V^*	maximum volatiles fraction released from coal particles
V_r^*	actual ultimate yield
V_r^{**}	potential ultimate yield of the reactive volatiles
V_{nr}^*	the potential ultimate yield of the non-reactive volatiles
V_b	bed volume (m ³)
V_b	bubble volume
V_b	volume of the bed (m ³)
V_c	volume of the unreacted CaCO ₃ core (m ³)
V_{cc}	molar volume of CaCO ₃ (m ³ /mol)
V_F	volume of the SO ₂ mass transfer film (m ³)
V_i	volatiles pseudo-species fraction

V_p	volume of the particle (m^3)
X	cross flow factor, $=Q_b H/u_a V_b$
$\bar{x}$	mean of x values for slope statistical analysis
X_c	extent of calcination ($100 \cdot \text{mol CO}_2 \text{ released} / \text{mol Ca, \%}$)
X_s	extent of sulfation ($100 \cdot \text{mol SO}_2 \text{ absorbed} / \text{mol Ca, \%}$)
$y(t)$	dynamic system response function
y_i	constant mole fraction of CO_2

Greek letters

α	coefficient in devolatilization rate power law for a fluidized bed (s)
β	Ca/S ratio
δ	Dirac delta function
ϵ_b	bed voidage, volume fluid in bed/ volume of bed
ϵ_c	dimensionless core radius $= r_c/r_p$
ϵ_i	residual value
ϵ_p	particle emissivity
ϵ_p	particle void
ϵ_s	effectiveness factor for sulfation
ϕ	mechanism factor in char combustion rate constant
ϕ_s	product layer diffusion Thiele modulus for sulfation
η_s	fractional reduction in SO_2 emissions vs. no limestone addition
ν	exponent in devolatilization rate power law
ν	kinematic viscosity (m^2/s)

ρ_c	density of char particle (g/m^3)
ρ_{CaO}	density of lime (g/m^3)
ρ_{ls}	density of limestone (g/m^3)
ρ_{p0}	original particle density
σ	standard deviation
σ	Stefan-Boltzmann radiation constant
τ_c	calcination time constant (s)
τ_c	characteristic char burnout time (s)
τ_{cb}	calcination time constant for bulk mass transfer-controlled calcination (s)
τ_{cbd}	calcination time constant for bulk mass transfer-controlled calcination with pore diffusion as a secondary resistance (s)
τ_{cbk}	calcination time constant for bulk mass transfer-controlled calcination with chemistry as a secondary resistance (s)
τ_{cd}	calcination time constant for pore diffusion-controlled calcination (s)
τ_{ch}	calcination time constant for film diffusion-controlled calcination (s)
τ_{ck}	calcination time constant for chemistry-controlled calcination (s)
τ_e	elutriation time constant (s)
τ_i	contribution of interphase mass transfer of O_2 between bubble and emulsion phase to the characteristic char burnout time (s)
τ_i	instrument time constant (s)
τ_i	instrument time constant (s)
τ_p	pore plugging time constant (s)
τ_s	sulfation time constant (s)
τ_{sb}	sulfation time constant for bulk mass transfer-controlled sulfation (s)
τ_{sbd}	sulfation time constant for bulk mass transfer-controlled sulfation with pore diffusion as a secondary resistance (s)

τ_{sbk}	sulfation time constant for bulk mass transfer-controlled sulfation with chemistry as a secondary resistance (s)
τ_{sd}	sulfation time constant for pore diffusion-controlled sulfation (s)
τ_{sh}	sulfation time constant for film diffusion-controlled sulfation (s)
τ_{sk}	sulfation time constant for chemistry-controlled sulfation (s)
τ_v	characteristic volatiles release time (s)
ω	frequency
Ω	$u-(u-u_0)\exp(-X)$
ξ_s	dimensionless radius of CaO core during sulfation = r_{sc}/r_p

EXECUTIVE SUMMARY

The objective of this project was to develop methods for characterizing fuels and sorbents from time-series data obtained during transient operation of fluidized bed boilers. These methods aimed at determining time constants for devolatilization and char burnout using carbon dioxide (CO_2) profiles and from time constants for the calcination and sulfation processes using CO_2 and sulfur dioxide (SO_2) profiles. The objective was approached in two phases of work.

Laboratory-scale experiments

The first phase performed tests in a laboratory-scale bubbling fluidized bed combustor (FBC) at Iowa State University. The purpose of this phase was to develop in-situ methods for evaluating coal and sorbent properties by detecting fluctuations in exhaust gas emissions after perturbing the feedstock entering the combustor. In Phase 1 it was shown that transient gas emissions from fluidized bed combustors could be used to obtain information on combustor dynamics. Carbon dioxide, SO_2 , and carbon monoxide (CO) emissions were used to determine rates of coal devolatilization, char burning, and limestone calcination and sulfation. Analysis of these emission profiles was done both in the time domain and in the frequency domain.

Estimates of devolatilization times for particles larger than 3 mm were comparable to values described by other researchers. Devolatilization times for smaller particles were affected by a significant lag in the sampling system.

For char combustion, the hypothesis of intrinsic chemical kinetics being rate limiting was not supported by tests performed in the laboratory combustor. An Indiana bituminous coal used in these tests fragmented during volatiles release, resulting in fragments that burned much faster than the original particles. It was hypothesized that primary fragmentation is responsible for the smaller than expected exponent in the power law for char burning. These results highlight the importance of fragmentation in understanding burning rates under realistic combustion conditions. This study suggests that particle distributions, even narrow distributions, significantly affect the

transient response of coal combustion in a fluidized bed. Furthermore, this study represents a unified theory that explains the wide differences observed between the impulse responses of small and large particles.

Calcination was modeled by a shrinking particle core model and found to be largely controlled by the chemical reaction rate. Observed activation energies from laboratory-scale experiments are slightly smaller than those in the literature for chemistry-rate-controlled calcination of smaller particles. The size dependence for the calcination time constant was greater than one, which suggests some influence of pore diffusion on the calcination process for larger particles at higher temperatures. Experimental results also show that the chemical reaction rate is a function of the partial pressure of CO_2 and the equilibrium partial pressure for calcination. In most cases the extent of calcination was close to 80%.

Particle analysis gave indications of a loss of surface area during the calcination process. Surface area loss may present itself by an increased sulfation reaction rate early in the transient, when the outer edge of the particle is undergoing calcination. Surface area testing shows that at higher temperatures, surface area and pore volume are lower, while the mean pore radius is higher.

Because of pore-plugging, the sulfation process was successfully modeled as a shrinking particle core with an exponentially decaying diffusivity. Although pore plugging ultimately controlled sulfation, at early times laboratory experiments showed mixed control. At these times, film diffusion and bed mixing contribute significant resistances to reaction. The reaction was not controlled by the chemical reaction rate at any condition tested in the laboratory-scale FBC. The influence of temperature on the extent of sulfation was smaller than is reported in the literature and was also smaller than expected for sulfation in the full-scale combustor. Cedar Bay #1 limestone exhibited higher extents of sulfation than the Gilmore City formation limestone from the I.S.U. power plant. The performance of Nova Scotia limestone was worse than either of the other limestones.

Full-scale boiler experiments

Phase 2 involved configuring the ISU Physical Plant Number 2 circulating fluidized bed (CFB) boiler for dynamic tests from coal and sorbent batch additions. The analytical methods developed in Phase 1 were applied to tests on the full scale boiler in Phase 2. Preliminary feasibility testing used the plant's continuous emissions monitoring (CEM) equipment to determine the approximate batch size needed, the required location of measuring equipment, and steadiness of the CO_2 and SO_2 signals. A Fourier Transform Infrared (FTIR) spectrometer was installed to sample gas at the exit of the boiler cyclone. The FTIR spectrometer yielded time-dependent gas concentrations that could not be detected by the plant's CEM equipment. Tests were done by batching coal and limestone into the boiler through a rapid-dump coal hopper installed at the end of one of the boiler's two coal drag conveyors.

The FTIR is a powerful tool for studying coal combustion processes in an on-line CFB boiler. Circulating fluidized bed combustion dynamics are complex compared to the bubbling fluidized bed combustor. It is believed that staged combustion has an influence on some of the parameters studied here, but the specific impact could not be determined due to the limitation of having only one sampling point at the cyclone outlet. A noisy steady-state flow of coal due to intermittent clumps of coal entering from the coal-feed drag conveyor inhibited signal analysis. The presence of CO and methane indicated oxygen starvation occurred during devolatilization, at least locally to the particles.

In contrast to laboratory results, char burnout in the power plant boiler did not begin until devolatilization was complete. Devolatilization time was found to be proportional to $d_i^{0.73}$. The char time constant was proportional to $d_i^{0.54}$, or $d_i^{0.55}$, depending on the method used to calculate it. This result suggests that char combustion is controlled by chemical kinetics with primary fragmentation. The burning rate of single particles was also studied. The burning rate is expected to be proportional to d_i for diffusion control and proportional to d_i^2 for chemical-kinetics control. This work found the burning rate to be proportional to $d_i^{2.58}$ which suggests chemical-kinetics control with primary fragmentation.

Spectral analysis

Spectral analysis was developed as a new method of determining char and devolatilization time constants from the transient CO₂ emissions from coal combustion. The Bode plot obtained from spectral analysis was consistent with the assumption of rapid exponential devolatilization decay and slower exponential CO₂ decay during char burning, at least for the bubbling bed data. Bode plots revealed two distinct cornering frequencies, corresponding to devolatilization and char time constants. However, it was shown that a data set of minimum time length must be recorded if spectral analysis is to be used successfully.

For the bubbling bed combustor, the time constants calculated with spectral analysis were in good agreement with those calculated using time domain methods for small particles, where the time length of the data set was adequate. However, it was found that the time constants calculated with spectral analysis were consistently smaller than those calculated with time-domain methods for the largest particles, indicating the lengths of the data sets were too short. An order-of-magnitude estimate is required of char time constants to ensure that sufficient data are taken for successful spectral analysis. The background fluctuations in the CFB CO₂ data precluded its use for spectral analysis, as the "noise" introduced by the high frequency background fluctuations masked the actual spectral features.

Spectral analysis was not used in the calcination or sulfation analyses for two reasons. The non-linear nature of the sulfation reaction did not allow interpretation within the framework of inherently linear Bode plots. Furthermore, the large amount of correlated noise from the uneven coal feed masked the signals of interest.

1. INTRODUCTION

The objective of this project was to develop methods for characterizing fuels and sorbents from time-series data obtained during transient operation of fluidized bed boilers. These methods aimed at determining time constants for devolatilization and char burnout from carbon dioxide (CO_2) profiles and time constants for the calcination and sulfation processes from CO_2 and sulfur dioxide (SO_2) profiles. The objective was approached in two phases of work.

The first phase performed tests on a bench-scale laboratory bubbling fluidized bed combustor (FBC) at Iowa State University. The purpose of this phase was to develop in-situ methods for evaluating coal and sorbent properties by detecting fluctuations in exhaust gas emissions after perturbing the feedstock entering the combustor. In Phase 1 it was shown that transient gas emissions from fluidized bed combustors could be used to obtain information on combustor dynamics. Carbon dioxide, SO_2 , and carbon monoxide (CO) emissions were used to determine rates of coal devolatilization, char burning, and limestone calcination and sulfation. Analysis of these emission profiles was done both in the time domain and in the frequency domain.

Phase 2 involved configuring the ISU Physical Plant Number 2 circulating fluidized bed (CFB) boiler for dynamic tests from coal and sorbent batch additions. The analytical methods developed in Phase 1 were applied to tests on the full scale boiler in Phase 2. Preliminary feasibility testing used the plant's continuous emissions monitoring (CEM) equipment to determine the approximate batch size needed, the required location of measuring equipment, and steadiness of the CO_2 and SO_2 signals. A Fourier Transform Infrared (FTIR) spectrometer was installed to sample from the exit of the boiler cyclone. The FTIR spectrometer yielded time-dependent gas concentrations that could not be detected by the plant's CEM equipment. Tests were done by batching coal and limestone into the boiler through a rapid-dump coal hopper installed at the end of one of the boiler's two coal drag conveyors.

2. THEORETICAL DEVELOPMENT

2.1 Devolatilization model

Devolatilization is the release of volatile matter from coal particles upon heating to high temperatures. There is evidence that devolatilization is a chemical decomposition reaction [1]. The maximum volatiles yield, V^* , is a strong function of temperature. A number of devolatilization models have been proposed which have been reviewed by Howard [2]. The simplest of these is a first order reaction model [3, 4]:

$$\frac{dV}{dt} = \frac{V^* - V}{\tau_v} \quad (2.1)$$

where the characteristic time for devolatilization, τ_v , is assumed to follow the Arrhenius form:

$$\frac{1}{\tau_v} = A \exp\left(-\frac{E_v}{RT}\right) \quad (2.2)$$

Since pyrolysis (devolatilization carried out under reducing conditions) consists of a large number of parallel reactions [2] this model has been criticized as an oversimplification of the complicated pyrolysis process. A more accurate representation of pyrolysis rewrites Eqn. (2.1) as a system of first order differential equations, each representing a different pyrolysis reaction with distinct activation energy. However, Anthony et al. [5] have shown that this system can be approximated by a single reaction model with a single activation energy. Equation (2.1) was adopted for the present study and found to adequately represent the data.

Recent research [3, 4, 6, 7, 8, 9,] has shown that, for particles larger than 100 μm , the characteristic devolatilization time, τ_v , depends strongly on the initial particle size, which indicates that heat and/or mass transfer, rather than chemical kinetics, is the rate-limiting process in

devolatilization. A commonly used relationship between the volatiles release time, t_v , and the initial coal particle size, d_i , is:

$$t_v = a d_i^v \quad (2.3)$$

Since 95% of the volatiles are released within three characteristic time constants [10], the devolatilization time of Eqn. (2.3) can be approximated as:

$$t_v = 3\tau_v \quad (2.4)$$

Essenhugh [6] determined volatile release times by observing the extinction of flames from single coal particles. He showed, for particles in the range 0.3 to 5 mm initial diameter, that t_v is proportional to the square of the particle diameter with the factor a equal to $0.9 \text{ mm}^2/\text{s}$ and that both a and v are independent of coal rank. Ragland and Weiss [8] also observed the extinction of flames from coal particles and estimated both a and v to be 1.5 for particles in the range 2 to 12 mm. Pillai [7], on the other hand, measured devolatilization times for two different coals in fluidized beds and found the exponent v to vary from 0.83 to 1.8, depending on coal type for particles smaller than 8 mm.

The experimental method of this study involved batching coal samples into a heated fluidized bed combustor or boiler. Transient CO_2 profiles vs. time for the batch tests were obtained and analyzed to determine the characteristic time constant for devolatilization, τ_v .

The overall reactor was treated as a continuously stirred tank reactor (CSTR). This assumption was validated by a series of step tests on the lab combustor using CO_2 injected into the base of the bed as a tracer gas. The CO_2 concentration exiting the overall reactor, $[\text{CO}_2]_R$, as a result of coal combustion is given by the mass balance:

$$v_b \frac{d[CO_2]_R}{dt} + Q[CO_2]_R = -\frac{1}{M_c} \left|_{\text{devol.}} - \frac{1}{M_c} \frac{dm}{dt} \right|_{\text{char}} \quad (2.5)$$

where the first term on the right hand side of Eqn. (2.5) is the rate that volatiles are converted to CO_2 and the second term is the rate that the carbon in the char is converted to CO_2 .

Carbon compounds released during devolatilization are assumed to be instantaneously oxidized to CO_2 . Accordingly, the rate of CO_2 formation from volatiles is given by the first-order devolatilization model:

$$-\frac{1}{M_c} \frac{dm}{dt} = Ng_o \exp\left(-\frac{t}{\tau_v}\right) \quad (2.6)$$

For time $t < 3\tau_v$, Eqn. (2.6) can be integrated and arranged to yield:

$$[CO_2]_R = [CO_2]_f + ([CO_2]_i - [CO_2]_f) \exp(-t/\tau_v) \quad (2.7)$$

where

$$[CO_2]_f = Nd_i^2 k [O_2]_e / Q \quad (2.8)$$

is the approximately constant contribution of char combustion to the CO_2 signal during devolatilization, $[CO_2]_i$ is the combined effect of devolatilization and char burning extrapolated to the starting time [11], and

$$Ng_o = Q \{ [CO_2]_i - [CO_2]_f \}. \quad (2.9)$$

The quantity $[CO_2]_i$ is given by:

$$[CO_2]_i = \frac{N}{Q} (g_o + kd_i^2 [O_2]_e) \quad (2.10)$$

Simultaneous char and volatiles combustion is assumed for Eqn. (2.7). Saxena [1] and Ragland and Weiss [8] theorize that char combustion does not begin until volatiles evolution is complete, as the oxygen cannot diffuse to the coal surface while the volatiles are being expelled. On the other hand, Christofides and Brown [11] demonstrated in their experiments in a laboratory-scale, bubbling fluidized bed combustor that char burned simultaneously with volatiles release.

Analysis of gas emissions from the combustor must account for the lag time associated with the gas sampling system and gas analyzers. Tracer gas tests suggest that a single lag time, called the instrumentation lag time, τ_I , can describe the composite behavior of the gas sampling and gas analyzer systems. The transient CO_2 signal registered at the gas analyzer, $[CO_2]_A$, is described by:

$$\frac{d[CO_2]_A}{dt} = -\frac{1}{\tau_I} \{ [CO_2]_R - [CO_2]_A \} \quad (2.11)$$

The experiments and experimental apparatus attempted to make τ_I very small, under which circumstances the analyzer registers the reactor concentration and the subscript designation can be dropped. This goal of keeping τ_I negligibly small was not always obtained.

One of the goals was to obtain devolatilization and char burnout rates from CO_2 profiles. In the case of devolatilization, it was desired to find τ_v . It was noted that char consumption was very slow compared to both gas advection through the fluidized bed and devolatilization of gases from coal particles. Further, it was assumed that a quasi-steady process was established between CO_2 formed from volatiles and CO_2 removed by gas advection. Accordingly, for $V_b/Q < t < 3\tau_v$, Eqn.(2.5) can be integrated to yield:

$$\frac{[\text{CO}_2]_R - [\text{CO}_2]_f}{[\text{CO}_2]_i - [\text{CO}_2]_f} = \exp\left(-\frac{t}{\tau_v}\right) \quad (2.12)$$

where $[\text{CO}_2]_f$ is the approximately constant contribution of char combustion to the CO_2 signal during devolatilization, and $[\text{CO}_2]_i$ is the combined effect of devolatilization and char burning extrapolated to the starting time.

Equation (2.12) assumes that devolatilization and char burning occur simultaneously. Saxena [1] and Ragland and Weiss [8] have suggested that char consumption does not begin until after devolatilization, an idea that assumes oxygen cannot diffuse to the coal particle surface while volatiles are being expelled. Under such circumstances, $[\text{CO}_2]_f$ would be zero in Eqn. (2.12).

2.2 Char burnout model

Char burnout time is also a strong function of the particle size [12, 13]. Avedesian and Davidson [12] were among the first to investigate char burning in fluidized beds. They developed a model that explained why the char burnout time, t_c , for large particles was proportional to the square of particle diameter in their experiments. Ross and Davidson [13] improved this model by introducing the effects of chemical reaction on burnout time:

$$t_c = \frac{m_i}{12[\text{O}_2]_i A_b [u - (u - u_o)e^{-x}]} + \frac{\rho_c d_i}{24 k_0 [\text{O}_2]_i} + \frac{\rho_c d_i^2}{48 \text{Sh} D_m [\text{O}_2]_i} \quad (2.13)$$

The first term on the right hand side of Eqn. (2.13), denoted as t_i , is the time associated with interphase transport of oxygen between the bubble and emulsion phases of the bubbling fluidized bed. The second and third terms are associated with chemical kinetics and film diffusion (constant Sherwood number) contributions to char burnout time, respectively. The controlling mechanism is dependent on the particle size. Much evidence suggests that chemical reaction dominates for particles smaller than 100 μm , whereas mass diffusion controls the reaction rate for

particles larger than 1 mm [12, 13]. More comprehensive models, as reviewed by Essenhigh [14], consider additional resistances to the overall burning rate. However, interphase mass transport, chemical kinetics, and film diffusion are thought to be the most important resistances under conditions of bubbling bed combustion.

Several researchers [12-14] measured char burnout times in fluidized beds by observing and timing the particles as they burned. Burnout time for large coal particles is known to decrease substantially if particles fragment during devolatilization or char combustion [6, 8, 15, 16].

It is convenient to introduce the concept of characteristic time for char combustion. As will be shown, for sufficiently short times, char combustion can be modeled as a first-order process with characteristic time constant, τ_c . This characteristic time will be related to char burnout time in a later section.

Char consumption is assumed to occur in the emulsion phase and follow the first-order oxidation reaction:

$$-\frac{1}{M_c} \frac{dm}{dt} \Big|_{\text{char}} = N\pi d^2 k [O_2]_e \quad (2.14)$$

where the concentration of oxygen in the emulsion phase, $[O_2]_e$, is influenced by the rates of oxygen consumption and the interphase transport of oxygen from bubbles to the emulsion phase. Avedesian and Davidson [12] applied a quasi-steady assumption on oxygen mass balance to obtain an expression for $[O_2]_e$:

$$[O_2]_e = \frac{[O_2]_i}{kN\pi d_i^2 / (A_b \Omega) + 1} \quad (2.15)$$

where $[O_2]_i$ is the inlet concentration of oxygen entering the fluidized bed.

The overall char reaction rate constant, k , can have contributions from both film mass transfer and intrinsic chemical kinetics. For the present work, the overall reaction rate constant is presented by a power law:

$$k = a_o d^{1-n} \quad (2.16)$$

Although this power law is an oversimplification of the general case of char combustion, it well represents several rate-limiting cases shown in Table 2.1.

Char consumption is an extremely nonlinear process; a more complicated analysis is required to interpret the data. For times greater than $3\tau_v$ only char burning substantially contributes to the CO_2 profile. The quasi-steady assumption applied to Eqn. (2.5) now yields:

$$[CO_2]_R = - \frac{1}{QM_c} \frac{dm}{dt} \Big|_{char} = \frac{[O_2]_i}{Q} \left\{ \frac{kN\pi d^2}{kN\pi d_i^2 / (A_b \Omega) + 1} \right\} \quad (2.17)$$

where k depends on diameter according to Eqn. (2.16). For spherical particles ($m = N\rho_c \pi d^3/6$) Eqn. (2.17) can be rewritten in terms of diameter as:

$$[CO_2]_R = - \frac{1}{2} \frac{N\pi\rho_c d^2}{M_c} \frac{d(d)}{dt} \quad (2.18)$$

Assuming the spherical particles burn as shrinking cores, Eqn. (2.14) can be integrated to obtain a transcendental equation relating particle diameter to time:

$$\frac{1}{3} \frac{N\pi(d_i^3 - d^3)}{A_b \Omega} + \frac{1}{a_o} \left(\frac{1}{n} \right) (d_i^n - d^n) = \frac{2}{\rho_c} M_c [O_2]_i t \quad (2.19)$$

The burnout time, t_c , for char particles is obtained from Eqn. (2.19) by setting $d = 0$ and $t = t_c$:

$$t_c - t_i = \frac{\rho_c d_i^n}{2 n a_o M_c [O_2]_i} \quad (2.20)$$

where t_i , the contribution of interphase mass transport of O_2 between emulsion and bubble phase to the burnout time, is defined as:

$$t_i = \frac{m_i}{A_b \Omega M_c [O_2]_i} \quad (2.21)$$

In these experiments t_c was taken to be the time that the transient CO_2 signal was no longer detectable above the steady state background CO_2 level. Accordingly, t_c may be significantly underestimated for large, slow burning particles that do not generate strong CO_2 signals in the last stages of char burnout.

For times much shorter than the burnout time, it is convenient to linearize Eqn. (2.19):

$$\frac{d(t)}{d_i} = 1 - \frac{2 M_c [O_2]_i t / \rho_c}{N \pi d_i^3 / (A_b \Omega) + d_i^2 / a_o} \approx 1 - \frac{t}{\tau_c} \quad (2.22)$$

where τ_c , a characteristic time for char burning, is defined by:

$$\tau_c - t_i = \frac{\rho_c d_i^n}{2 a_o M_c [O_2]_i} \quad (2.23)$$

This linear model can also be expressed, for short combustion times, as an exponential decay:

$$\frac{d(t)}{d_i} \cong \exp(-t / \tau_c) \quad (2.24)$$

which is convenient for some data analysis. The contribution of interphase mass transfer of O_2 between bubble and emulsion phase (τ_i) to the characteristic time is defined by:

$$\tau_i \equiv \frac{3 m_i}{A_b \Omega M_c [O_2]_i} \quad (2.25)$$

Combining Eqns. (2.20) and (2.23) gives the relationship between t_c and τ_c :

$$\frac{t_c - t_i}{\tau_c - \tau_i} = \frac{1}{n} \quad (2.26)$$

where the value of n depends on the nature of the rate-limiting mechanism (Table 2.1).

For spherical particles burning as constant density shrinking cores the diameter is related to the mass as:

$$\frac{d(t)}{d_i} = \left(\frac{m(t)}{m_i} \right)^{1/3} \quad (2.27)$$

Where $m(t)$ represents the amount of carbon mass remaining in the char at time t , and m_i is the initial mass of char carbon.

Substituting Eqn. (2.27) for the diameter into Eqn. (2.18), the following expression for CO_2 concentration during char burning is obtained:

$$[CO_2]_R = \frac{N\pi\rho_c d_i}{2\tau_c} \exp\left(-\frac{t}{\tau_c/3}\right) \quad (2.28)$$

Combining Eqn. (2.7) with Eqn. (2.28) the CO_2 concentration beginning at the CO_2 peak during devolatilization can be modeled as:

$$[\text{CO}_2]_R = [\text{CO}_2]_{\text{avg}} + A \exp(-t/\tau_v) + B \exp(-t/(\tau_c)) \quad (2.29)$$

where $[\text{CO}_2]_{\text{avg}}$ is the steady state CO_2 background concentration. The coefficients A and B are defined as:

$$A = Q \{ [\text{CO}_2]_i - [\text{CO}_2]_f \} = N g_o \quad (2.30)$$

$$B = [\text{CO}_2]_f [\text{CO}_2]_{\text{avg}} = \frac{N \pi \rho_c d_i}{2 \tau_c} \quad (2.31)$$

2.3 Population balance model

The previous developments assumed monodispersed particle distributions. However, as will become apparent for some of the experimental results, recognizing that even screened coal samples are actually populations of particles of different sizes is important in explaining certain phenomena. In these circumstances, char combustion is better modeled through a mass distribution function, $\lambda(d, t)$. This distribution can be integrated with respect to particle diameter d to obtain the total mass of char in the bed at any time:

$$m_c(t) = \int_0^\infty \lambda(d, t) dd \quad (2.32)$$

A detailed description of the population balance equation is presented by Kunii and Levenspiel [17], and a partial solution for a monodispersed size distribution is presented by van der Post et al. [18]. Following the notation of van der Post et al. [18], a mass balance can be written for char particles in the interval d to $d + \Delta d$ [18], omitting carbon loss through attrition and secondary fragmentation for simplicity. By modeling burning char particles as constant density spheres whose diameters shrink at the rate $R(d)$, the mass balance equation is:

$$\begin{aligned} \frac{\partial}{\partial t} (\lambda(d, t) \Delta d) = & F(d, t) \Delta d - \lambda(d + \Delta d, t) \\ & \times R(d + \Delta d) + \lambda(d, t) R(d) + \frac{6\lambda(d, t) \Delta d}{\pi \rho_c d^3} \cdot \frac{\pi \rho_c d^2 R(d)}{2} \end{aligned} \quad (2.33)$$

where $F(d, t)$ is the feed of char per unit size into the bed. For a diffusion rate-limited process in which the surface reaction is effectively

$R(d)$ can be approximated by [12, 13]:

$$R(d) = -\frac{f}{d}, \quad f = \frac{24 \text{ Sh } D_{AB} C_p}{\rho_c} \quad (2.35)$$

This formulation has been revised to include chemical kinetics [13] and a variable Sherwood number [19]. Chemical kinetics become significant for particles smaller than 100 μm [12], which is far removed from the present work on 0.6 - 5.6 mm particles. On the other hand, for a diffusion-controlled reaction, a variable Sherwood number does not appreciably change the curvature of the impulse response. Consequently, a constant Sherwood number that characterizes the entire response is a reasonably good approximation [12]. Accordingly, with this approximation, Eqn. (2.35) can be substituted into Eqn. (2.33), which, after dividing each side by Δd and taking the limit as Δd approaches zero, reduces to [18]:

$$\frac{\partial}{\partial t} \lambda(d, t) = F(d, t) + \frac{\partial}{\partial d} \left[\frac{f}{d} \lambda(d, t) \right] - \frac{3f}{d^2} \lambda(d, t) \quad (2.36)$$

Equivalently,

$$\frac{\partial}{\partial t} \lambda(d, t) = F(d, t) + \frac{f}{d} \frac{\partial}{\partial d} \lambda(d, t) - \frac{4f}{d^2} \lambda(d, t) \quad (2.37)$$

The total rate of char consumption is found by integrating the rate of char consumption in the interval d to $d + \Delta d$ over all d :

$$K(t) = \int_0^{d_{\max}} \frac{3f\lambda(d, t)}{d^2} dd \quad (2.38)$$

Finally, assuming that combustion can be described by the overall chemical reaction Eqn. (2.34), CO_2 concentrations leaving the combustor are found by

$$[\text{CO}_2(t)]_c = \frac{K(t)}{M_c Q} \quad (2.39)$$

where Q is the volumetric air flow rate into the combustor and M_c is the molecular weight of carbon.

A closed-form solution to Eqn. (2.37) for a unit impulse in the feed rate of monodispersed size distribution was originally proposed by van der Post et al. [18]. Their solution is presented in the Laplace domain and is expanded in a Laurent series. From the Laurent series expansion, van der Post et al. [18] use a Pade approximation to model char combustion through a first-order, linear transfer function. However, in the time domain, their linear approximation and the analytical solution are incompatible. For example, their linear approximation has a positive-definite second derivative whereas the analytical solution has a negative-definite second derivative. As such, no physical significance can be attributed to their linear approximation. Although their analysis is flawed, it provides a useful basis for a nonlinear, time domain solution.

Impulse response for a monodispersed coal sample

For a system with zero initial conditions, Eqn. (2.37) can be transformed into the Laplace domain as:

$$\frac{\partial}{\partial d} \lambda(d, s) = -\frac{d}{f} D(d, s) + \left(\frac{4}{d} + \frac{d}{f} s \right) \lambda(d, s) \quad (2.40)$$

In general, $F(d, t)$ is the product of the coal feed rate per unit mass (s^{-1}) and mass distribution (g/mm) such that the integral of $F(d, t)$ with respect to d gives the total coal feed rate (g/s). For a monodispersed sample of coal, the mass distribution is described by a Dirac delta function. In the Laplace domain, $F(d, t)$ becomes:

$$F(d, s) = F_0(s) \delta(d_0 - d) \quad (2.41)$$

Note that the delta function argument is $(d_0 - d)$, not $(d - d_0)$. This distinction is important because the integral of feed distribution with respect to d must be non zero for d less than d_0 (i.e., particles shrink). Substituting Eqn. (2.41) into Eqn. (2.40) yields a first-order ordinary differential equation in d with the solution:

$$\lambda(d, s) = \frac{F_0(s) d^4}{f d_0^3} \exp \left[\frac{-s}{2f} (d_0^2 - d^2) \right] \times h(d_0 - d) \quad (2.42)$$

where $h(\bullet)$ is a Heaviside step function. For a unit impulse in the coal feed rate:

$$F_0(s) = 1 \quad (2.43)$$

Taking the inverse Laplace transform, a monodispersed particle distribution evolves through time as:

$$\lambda(d, t) = \frac{d^4}{fd_o^3} \delta\left(\frac{d_o^2 - d^2}{2f} - t\right) \quad (2.44)$$

When integrating over all d , Eqn. (2.44) reduces to the well-known square law for burning particles [12].

Impulse response for an arbitrarily sized coal sample

Equation (2.44) describes an impulse response for a monodispersed coal sample. This response can be generalized by integrating it over an initial particle distribution, $\phi(d_o)$. Consider an initial particle distribution that is non zero over $d_{\min} \leq d_o \leq d_{\max}$ and is zero otherwise. Multiplying Eqn. (2.42) by $\phi(d_o)$ and integrating the product over gives:

$$\lambda(d, t) = \int_{d_{\min}}^{d_{\max}} \phi(d_o) \frac{d^4}{fd_o^3} \times \delta\left(\frac{d_o^2 - d^2}{2f} - t\right) dd_o \quad (2.45)$$

With an appropriate change of variables, Eqn. (2.45) can be integrated to give:

$$\lambda(d, t) = \frac{\phi\left(\sqrt{d^2 + 2ft}\right) d^4}{\left(d^2 + 2ft\right)^2} \times h\left(\frac{d_{\max}^2 - d^2}{2f} - t\right) \times h\left(t - \frac{d_{\min}^2 - d^2}{2f}\right) \quad (2.46)$$

Char consumption for a block distribution

For these tests, "monodispersed" coal samples are formed by sieving coal particles between consecutive screen sizes. For example, coal sieved to 16x18 mesh has a maximum diameter of 1.18 mm and a minimum diameter of 1.00 mm. In this case,

$$d_{\min} = 0.85d_{\max} \quad (2.47)$$

which suggests that the particle distribution has a significant variance. Usually, the actual particle distribution of coal collected from consecutive screen sizes is unknown. However, if the distribution is narrow, it can be approximated as a block function:

$$\varphi(d_O) = \varphi_O, \quad d_{\min} \leq d_O \leq d_{\max} \quad (2.48)$$

$$\varphi(d_O) = 0, \quad \text{otherwise} \quad (2.49)$$

where φ_O is a constant. This distribution, in conjunction with Eqn. (2.46), can be substituted into Eqn. (2.38) to find the rate of char consumption. For:

$$d_{\max} > d_{\min} > 0 \quad (2.50)$$

the Heaviside functions in Eqn. (2.46) partition the impulse response into three distinct regions:

$$0 \leq t \leq \frac{d_{\min}^2}{2f} \quad (2.51)$$

$$\frac{d_{\min}^2}{2f} \leq t \leq \frac{d_{\max}^2}{2f} \quad (2.52)$$

$$t > \frac{d_{\max}^2}{2f} \quad (2.53)$$

The char consumption rate, $K(t)$, is uniformly continuous over the interval:

$$0 \leq t \leq \frac{d_{\max}^2}{2f} \quad (2.54)$$

For the interval of Eqn. (2.51), the solution is:

$$\begin{aligned}
K(t) = & \frac{3f\lambda\phi_o}{4\sqrt{ft} d_{\max}^2 d_{\min}^2} \times \left[\sqrt{2} d_{\max}^2 d_{\min}^2 \times \tan^{-1} \left(\left(\frac{1}{2} \right) \sqrt{\frac{2}{ft}} \sqrt{d_{\max}^2 - 2ft} \right) \right. \\
& - 2 d_{\min}^2 \sqrt{ft} \sqrt{d_{\max}^2 - 2ft} - \sqrt{2} d_{\max}^2 d_{\min}^2 \\
& \left. \times \tan^{-1} \left(\left(\frac{1}{2} \right) \sqrt{\frac{2}{ft}} \sqrt{d_{\min}^2 - 2ft} \right) + 2 d_{\max}^2 \sqrt{ft} \sqrt{d_{\min}^2 - 2ft} \right] \quad (2.55)
\end{aligned}$$

For the limits of Eqn. (2.52), the solution is:

$$\begin{aligned}
K(t) = & \frac{3f\phi_o}{4\sqrt{ft} d_{\max}^2} \times \left[\sqrt{2} d_{\max}^2 \times \tan^{-1} \left(\left(\frac{1}{2} \right) \sqrt{\frac{2}{ft}} \sqrt{d_{\max}^2 - 2ft} \right) \right. \\
& \left. - 2 \sqrt{ft} \sqrt{d_{\max}^2 - 2ft} \right] \quad (2.56)
\end{aligned}$$

and for the limits of Eqn. (2.53),

$$K(t) = 0. \quad (2.57)$$

2.4 Calcination model

Calcination theory

Although much has been written about the calcination reaction, there is significant variation in the data reported for reaction kinetics and thermodynamics. In the calcination of limestone, the sorbent releases CO_2 in an endothermic reaction:

The carbonation reaction, which is the reverse of Eqn. (2.58), is also significant at FBC operating temperatures, resulting in a reaction rate that includes the effects of the equilibrium partial pressure. The resulting calcine will vary considerably based on differences in the structure of the parent limestone, the types and magnitude of impurities present, the thermodynamic conditions, and the concentration of gases in the reactor. The variety of test conditions employed by researchers also influences the rate-controlling process reported in their studies.

Since the porosity of uncalcined limestones is negligible, the calcination reaction greatly affects the subsequent sulfation reaction. The degree of calcination and the properties of the CaO matrix determine the ability of the calcine to remove SO_2 . High concentrations of CO_2 in the reactor may decrease the degree of calcination in the sorbent due to the reverse reaction of Eqn. (2.58). Additionally, calcium sulfate (CaSO_4) deposits on the outer surface of the limestone particle may restrict the escape of CO_2 from the particle, and thus limit the extent of calcination.

Some researchers [20, 21] have concluded that calcination can be modeled as a shrinking particle core model, an idea that is further explored in chapter three. According to Khraisha and Dugwell [20], the overall reaction process using this model includes at least five steps:

- 1) heat transfer from the surrounding atmosphere to the particle surface
- 2) heat transfer from the particle surface to the reaction site
- 3) chemical reaction at the reaction site
- 4) diffusion of CO_2 from the reaction site through an ash layer to the particle surface, and
- 5) diffusion of CO_2 from the particle surface to the surrounding atmosphere.

For analysis in fluidized beds, step 5 is often subdivided into a film diffusion step from the particle surface to the particulate phase, and an interphase mass transfer step from the particulate phase to the bubbles [22].

The rate-controlling step in the calcination of limestone is the subject of debate. Many researchers [20, 22-24] have determined that the reaction is controlled by the chemical reaction step at the reaction interface. Khraisha and Dugwell [20] report that the reaction is chemically controlled, but that the particle temperature was dependent on heat transfer from the reactor to

the particle surface, rather than dependent on internal conduction. Hills [21] demonstrated that for 10 mm diameter spheres, which is a relatively large sorbent particle, the reaction was controlled by heat transfer to the reaction interface and mass transfer away from the reaction interface.

Rajeswara *et al.* [25] abandoned the more traditional shrinking core approach and analyzed the reaction using a grain model. They found that the assumption of an isothermal particle is not valid. In their analysis, the radial temperature variation is considered through the use of a steady state relationship developed by Prater [26]. To validate their analysis, they measured the temperature of a 6 mm diameter pellet at a location 1 mm below its surface. Temperature at this location dropped from 1150 K to 1090 K during the endothermic calcination reaction. From their analysis they found radial temperature variations of 40 K through the pellet. The use of large (6 mm) manufactured pellets may impact the usefulness of their analysis for FBC boilers, which use raw limestone with smaller particle diameters.

Dennis and Hayhurst [22] argue that interphase mass transfer cannot be controlling since the reaction radius decreases linearly with time. They also calculated the maximum temperature difference by equating conduction heat transfer through the CaO layer to the heat absorbed through the calcination reaction. Using values from the literature for thermal conductivity [27] and heat of calcination [21], they found that the maximum temperature difference across the particle is 11 K. From this they dismissed conduction through the CaO ash layer as a rate-limiting mechanism. Nevertheless, they concede that interphase heat transfer can act as a resistance to reaction. In their model, they include only the chemical reaction step and the pore diffusion step. They develop an expression for the calcination reaction rate, which is a function of the equilibrium and instantaneous partial pressures of CO_2 , the total pressure and a fixed mole fraction of CO_2 .

Several researchers have shown that the specific surface area of the calcine is reduced at higher temperatures and concentrations of CO_2 and H_2O [28-30]. Stouffer and Yoon [30] calcined 100 mesh limestone samples in air at temperatures of 975 K, 1075 K, and 1175 K. They found that BET surface area is created more quickly at higher temperatures than at lower

temperatures. At higher temperatures, however, a rapid reduction in surface area occurs shortly after it is created. The net effect is that limestone calcined at higher temperatures develops less surface area. For limestone calcined at 1175 K, the surface area after two minutes was 50 m²/g, but then it diminished to 33 m²/g after 10 minutes, and 25 m²/g after 30 minutes. Milne *et al.* [28] analyzed data from Borgwardt [31] and found substantially higher sintering rates in atmospheres containing H₂O and CO₂, than in N₂ atmospheres. They also found that the effects of H₂O and CO₂ were additive.

Calcination model

Many calcination models are variations of the shrinking core model (SCM) introduced by Yagi and Kunii [32] as described in Levenspiel [33]. The basic SCM consists of a chemical reaction at a receding particle core, diffusion through the outer portion of the particle, and diffusion through a gas film surrounding the particle. The time-rate-of-change of the flux of the diffusing species, based on the unchanging exterior surface of the particle, can be written as:

$$-\frac{1}{a_p} \frac{dN_A}{dt} = \frac{C_A}{R_{\text{film diffusion}} + R_{\text{pore diffusion}} + R_{\text{chemical reaction}}} \quad (2.59)$$

In equation (2.59), the resistances are functions of the film mass transfer coefficient, h , the chemical reaction rate coefficient, k , the effective diffusivity through the particle, D_e , and the radii of the particle and of the core, r_p and r_c , respectively. The SCM is a sum of resistances model, and is analogous to an electrical or heat transfer sum-of-resistances approach, involving a flux, a potential and a network of resistances in series.

Many investigators have concluded that calcination is controlled by a chemical reaction step at the interface of CaCO₃ and CaO, but some others have suggested control by heat transfer and mass transfer from the interface [21]. Dennis and Hayhurst [22] used a sum-of-resistances model that included ash diffusion and chemical reaction resistances. They developed an equation

for the calcination reaction time, t_c , which was simplified by showing that the diffusion resistance is much less than the chemical reaction resistance for pressures up to 3 bar. Their final equation is for chemical control, with chemical reaction rate driven by the difference between CO_2 partial pressure and the equilibrium pressure for the calcination and the carbonation reactions. Their final equation for the time to complete calcination is:

$$t_c = \frac{r_p}{k^* V_{\text{CaCO}_3} (p_E - p_R - y^* P)}, \quad (2.60)$$

where k^* is the chemistry rate constant for the backward, or carbonation, reaction, V_{CaCO_3} is the molar volume of CaCO_3 , p_E is the equilibrium partial pressure, p_R is the instantaneous partial pressure of CO_2 , P is the total pressure, and y^* is a constant mole fraction of CO_2 , which is determined from regression analysis of the data. The rate constant for calcination used for comparison to other values in the literature is the term $k^* p_E$.

Rajeswara Rao *et al.* [25] describe a slightly more complicated model. Their model is a grain model, which accounts for temperature differences within the particle. They use a set of two partial differential equations to describe diffusion and reaction in the solid pellet and in the grain. A relationship for temperature that includes external film resistances, as well as internal conduction and mass transfer, accompanies these equations. This equation for temperature takes on the following form:

$$T = T_o - \frac{h_c \Delta H}{h_T} ([\text{CO}_2]_S - [\text{CO}_2]_R) - \frac{D_e \Delta H}{k_c^*} ([\text{CO}_2] - [\text{CO}_2]_S) \quad (2.61)$$

where h_T is the heat transfer coefficient; k_c^* is the particle thermal conductivity; ΔH is the heat of reaction; and $[\text{CO}_2]_R$, $[\text{CO}_2]_S$, and $[\text{CO}_2]$ are concentrations of CO_2 in the combustor, at the particle surface, and in the particle as a function of radius, respectively.

The approach to the present study assumes an isothermal shrinking particle core model that includes chemical reaction, diffusion of CO₂ through a product layer, film mass transfer away from the particle, and bulk mass transfer in the bed. Assuming a continuously stirred tank reactor (CSTR), mass balances in the reactor result in a set of four differential equations for the core radius and for concentrations of CO₂ in the reactor, at the particle surface and at the unreacted core:

$$V_R \frac{d[CO_2]_R}{dt} = -Q\{[CO_2]_R - [CO_2]_I\} + h_c a_p \{[CO_2]_S - [CO_2]_R\} \quad (2.62)$$

$$V_p \frac{d[CO_2]_S}{dt} = -h_c a_p \{[CO_2]_S - [CO_2]_R\} + 4\pi \frac{D_{ec}}{\frac{1}{r_p} - \frac{1}{r_{cc}}} \{[CO_2]_S - [CO_2]_{cc}\} \quad (2.63)$$

$$V_c \frac{d[CO_2]_{cc}}{dt} = 4\pi \frac{D_{ec}}{\frac{1}{r_p} - \frac{1}{r_{cc}}} \{[CO_2]_{cc} - [CO_2]_S\} + k_c a_{cc} \{[CO_2]_E - [CO_2]_{cc}\} \quad (2.64)$$

$$\frac{dr_{cc}}{dt} = -\frac{k_c M_L}{\rho_L} \{[CO_2]_E - [CO_2]_{cc}\} \quad (2.65)$$

where [CO₂]_I and [CO₂]_{cc} are the concentrations of CO₂ at the inlet and at the unreacted CaCO₃ core, respectively. This system of ordinary differential equations will be referred to as the "full model" in subsequent discussions. The equilibrium concentration is determined by ideal gas conversion from the equilibrium partial pressure, i.e. [CO₂]_E = p_E/RT_{bed}. The equilibrium partial pressure is determined from an analysis by Baker *et al.* [34] which results in the partial pressure for the calcination equilibrium (in atmospheres) equal to:

$$\log_{10} p_E = -\frac{8308}{T} + 7.079. \quad (2.66)$$

If a quasi-steady approximation is applied to this model, time derivatives of $[CO_2]$ are set equal to zero, and the model simplifies to one ordinary differential equation and one algebraic equation:

$$-\frac{dr_{cc}}{dt} = \frac{\{[CO_2]_E - [CO_2]_I\} \frac{M_{LS}}{f_{CaCO_3} \rho_{LS}}}{\frac{3m_{LS}}{Q\rho_{LS}r_p} \frac{r_{cc}^2}{r_p^2} + \frac{1}{h_c} \frac{r_{cc}^2}{r_p^2} + \frac{(r_p - r_{cc})r_{cc}}{D_{ec}r_p} + \frac{1}{k_c}} \quad (2.67)$$

$$\frac{[CO_2]_E - [CO_2]_R}{[CO_2]_E - [CO_2]_I} = \frac{1}{1 + \frac{3m_{LS}}{Q\rho_{LS}r_p} \left(\frac{1}{\frac{1}{h_c} + \frac{(r_p - r_{cc})r_p}{D_{ec}r_{cc}} + \frac{1}{k_c} \frac{r_p^2}{r_{cc}^2}} \right)} \quad (2.68)$$

This model can be easily extended to non-spherical particles by introducing a shape factor, S , which is equal to 3 for spheres, 2 for cylinders and 1 for flat plates. A characteristic length, L , represents the particle radius for spheres and cylinders, and represents the half-thickness for flat plates. The ratio S/L is the ratio of surface area to volume for these particles. With these modifications, and defining ξ_c equal to r_{cc}/r_p , Eqns. (2.67) and (2.68) become:

$$-\frac{d\xi_c}{dt} = \frac{\{[CO_2]_E - [CO_2]_I\} \frac{M_{LS}}{f_{CaCO_3} \rho_{LS} L}}{\frac{Sm_{LS}}{Q\rho_{LS}L} \xi_c^{(S-1)} + \frac{1}{h_c} \xi_c^{(S-1)} + \frac{L(1-\xi_c)\xi_c^{(S-1)/2}}{D_{ec}} + \frac{1}{k_c}} \quad (2.69)$$

$$\frac{[CO_2]_E - [CO_2]_R}{[CO_2]_E - [CO_2]_I} = \frac{1}{1 + \frac{Sm_{LS}}{Q\rho_{LS}L} \left(\frac{1}{\frac{1}{h_c} + \frac{L(1-\xi_c)}{D_{ec}\xi_c(S-1)/2} + \frac{1}{k_c\xi_c(S-1)}} \right)} \quad (2.70)$$

These equations can also be derived by assuming a sum-of-resistances model as considered in Levenspiel [33], with the inclusion of a CSTR bed mixing resistance. If one of the resistances in Eqns (2.69) and (2.70) is considerably larger than the others, then limiting behavior is observed.

Calcination model simplification for limiting behavior

An objective of this investigation is to find time constants to characterize sorbent reactions analytically through time series or spectral methods. The shrinking core model of Eqns. (2.69) and (2.70) is useful in analyzing the transients, but numerical solution is required. The model can be simplified further by assuming rate-limiting mechanisms. To simplify the expressions, two constants are defined: $c_{1c} = \{[CO_2]_E - [CO_2]_I\}M_{LS}/f_{LS}\rho_{LS}$, and $c_2 = Sm/\rho_{LS}Q$. For the present discussion, analysis will be for spheres ($S = 3$) unless otherwise indicated. The four possible controlling mechanisms that can be examined by this model are: chemical reaction rate, film diffusion, pore diffusion, and bulk mass transfer. The following analysis addresses each of these possibilities.

Chemical reaction control

If chemical reaction is the controlling mechanism, the chemical reaction resistance term in Eqns. (2.69) and (2.70) is larger than the other resistances, so that the equations may be rewritten:

$$-\frac{d\xi_c}{dt} = \frac{c_{1c}}{L} k_c \quad (2.71)$$

$$\frac{[CO_2]_E - [CO_2]_R}{[CO_2]_E - [CO_2]_I} = \frac{1}{1 + \frac{c_2}{L} k_c \xi_c^2} \quad (2.72)$$

Equation (2.71) can be integrated directly to yield:

$$\xi_c = 1 - \frac{c_{1c}}{L} k_c t \quad (2.73)$$

which is the first two terms of the Taylor series expansion for the exponential function.

Consequently, for short times ξ_c may be approximated by:

$$\xi_c = e^{(-t/\tau_{ck})} \quad (2.74)$$

where $\tau_{ck} = L/k_c c_{1c}$. Substituting this result into Eqn. (2.72) and inverting the equation results in:

$$\frac{[CO_2]_E - [CO_2]_I}{[CO_2]_E - [CO_2]_R} - 1 = \frac{c_2 k_c}{L} e^{-2t/\tau_{ck}} \quad (2.75)$$

Recognizing that $[CO_2]_R$ is equal to $[CO_2]_O$ at time zero, the equation takes on the form:

$$\frac{\{[CO_2]_E - [CO_2]_O\}\{[CO_2]_R - [CO_2]_I\}}{\{[CO_2]_E - [CO_2]_R\}\{[CO_2]_O - [CO_2]_I\}} = e^{-t/\tau_c} \quad (2.76)$$

where $\tau_c = \tau_{ck}/2 = r_p/2k_c c_{1c}$. For equilibrium concentrations substantially larger than the reactor concentrations, Eqn. (2.76) is approximated by:

$$\frac{\{[CO_2]_R - [CO_2]_I\}}{\{[CO_2]_O - [CO_2]_I\}} = e^{-t/\tau_c} \quad (2.77)$$

This approximation gives approximately 5% error in the value of τ_c for atmospheric combustion at 1123 K.

The calcination time constant, τ_c , can be determined graphically from the slope of a log-linear plot of Eqn. (2.76). For chemistry controlled calcination, τ_c is directly proportional to L , which is r_p for the spherical particle shape. Additionally, it is seen that τ_c is inversely proportional to the reaction rate coefficient, k_c , and to $\{[CO_2]_E - [CO_2]_I\}$.

Comparison of the value of τ_c determined in this way for differing particle sizes, temperatures, and concentrations will indicate whether chemistry is the controlling mechanism. If τ_c is plotted versus particle diameter on a log-log plot, the slope will give the particle size dependence. For chemistry control, the slope should be equal to one. A log-linear plot of $1/\tau_c$ versus $1/T$ will yield the observed activation energy for calcination. If chemistry is controlling the observed activation energy should equal the true activation energy. If particle shapes other than spheres are used, the value of τ_c will also be proportional to $1/(S-1)$. For flat plates this results in an infinite value for τ_c , corresponding to a constant outlet concentration. For every shape, chemistry control results in an interface that recedes at a constant rate.

Film diffusion control

If calcination is controlled by diffusion through the gas film surrounding the particle, the film diffusion resistances will be much larger than the other resistances. For the film diffusion control case, Eqns (2.69) and (2.70) become:

$$-\frac{d\xi_c}{dt} = \frac{c_{1c}h_c}{L\xi_c^2} \quad (2.78)$$

$$\frac{[CO_2]_E - [CO_2]_R}{[CO_2]_E - [CO_2]_I} = \frac{1}{1 + \frac{c_2}{L}h_c} \quad (2.79)$$

Integration of Eqn. (2.78) yields:

$$\xi_c = \left(1 - \frac{3c_{lc}h_c}{L}t \right)^{1/3} \quad (2.80)$$

and application of the Taylor series expansion of the exponential function results in:

$$\xi_c = e^{-t / \tau_{ch}} \quad (2.81)$$

where $\tau_{ch} = L/h_c c_{lc}$. Equation (2.79) shows that the concentration transient is constant with time for film diffusion control. This response has not been observed in laboratory experiments nor in the literature. Although film diffusion may play a role in the calcination process, it clearly does not act as the controlling mechanism.

Pore diffusion control

To illustrate the effect of pore diffusion control, analysis is done for flat plates, utilizing the inherently simpler mathematics for this shape. For pore diffusion control Eqn. (2.69) becomes:

$$-\frac{d\xi_c}{dt} = \frac{D_{ec}c_{lc}}{L^2(1-\xi_c)} \quad (2.82)$$

Integration of Eqn. (2.82) yields:

$$(1 - \xi_c)^2 = \frac{2D_{ec}c_{lc}}{L^2}t = t/t_c \quad (2.83)$$

where t_c , the time to completely calcine the particle, is $L^2/(2D_{ec}c_{1c})$. The expression for the dimensionless core radius is:

$$\xi_c = 1 - \sqrt{\frac{t}{t_c}} \quad (2.84)$$

If pore diffusion is determined to be the controlling mechanism for calcination, the transient can be analyzed by writing Eqn. (2.70) for pore diffusion control:

$$\frac{[CO_2]_E - [CO_2]_I}{[CO_2]_E - [CO_2]_R} - 1 = \frac{c_2 D_{ec}}{L^2 (1 - \xi_c)} \quad (2.85)$$

Inversion and substitution of Eqn. (2.84) into Eqn. (2.85) yields:

$$\left(\frac{[CO_2]_E - [CO_2]_I}{[CO_2]_E - [CO_2]_R} - 1 \right)^{-1} = \left(\frac{[CO_2]_E - [CO_2]_I}{[CO_2]_R - [CO_2]_I} - 1 \right) = \frac{L^2}{c_2 D_{ec}} \sqrt{\frac{t}{t_c}} = \sqrt{\frac{t}{\tau_{cd}}} \quad (2.86)$$

where $\tau_{cd} = c_2^2 D_{ec} / 2c_{1c} L^2$. By making use of a Taylor series approximation, the linearized equation for short times is:

$$\left(\frac{[CO_2]_E - [CO_2]_I}{[CO_2]_R - [CO_2]_I} \right) = 1 + \left(\frac{t}{\tau_{cd}} \right)^{1/2} \cong e^{\sqrt{t/\tau_{cd}}} \quad (2.87)$$

Inverting once more, results in:

$$\left(\frac{[CO_2]_R - [CO_2]_I}{[CO_2]_E - [CO_2]_I} \right) = e^{-\sqrt{t/\tau_{cd}}} \quad (2.88)$$

The calcination time constant, τ_{cd} , can be determined from the reciprocal slope of a "log-squared"-linear plot:

$$\left\{ -\ln \left(\frac{[CO_2]_R - [CO_2]_I}{[CO_2]_O - [CO_2]_I} \right) \right\}^2 = \frac{1}{\tau_{cd}} t \quad (2.89)$$

Alternatively, Eqn. (2.86) results in a simple expression:

$$\left(\frac{[CO_2]_R - [CO_2]_I}{[CO_2]_E - [CO_2]_R} \right)^{-2} = \frac{1}{\tau_{cd}} t \quad (2.90)$$

which is valid for all times and can be plotted directly to fit a value of τ_{cd} .

Bulk mass transfer control

If bulk mass transfer is the controlling mechanism, bed mixing resistance ($3m_{LS}/\rho_{LS}Qr_p$) is significantly larger than the other resistances. For this case Eqn. (2.69) can be written:

$$-\frac{d\xi_c}{dt} = \frac{c_{1c}}{c_2 \xi_c^2} \quad (2.91)$$

Integrating and using the Taylor series expansion for the exponential function, Eqn. (2.91) becomes:

$$\xi_c = e^{-t / \tau_{cb}} \quad (2.92)$$

where $\tau_{cb} = c_2/c_{1c}$. Simplification of Eqn. (2.70) for bulk mass transfer control results in:

$$\frac{[CO_2]_E - [CO_2]_R}{[CO_2]_E - [CO_2]_I} = \frac{1}{1 + \frac{c_2}{L} K(t)} \quad (2.93)$$

In Eqn. (2.93), $K(t)$ is the overall reaction coefficient from the other resistances. Since the chemical and diffusion resistance terms are time dependent, $K(t)$ is written as a function of time. This allows for consideration of two cases in which bulk mass transfer is the primary controlling mechanism and either chemical reaction resistance or pore diffusion resistance is the secondary controlling mechanism.

For the case in which chemical reaction is the secondary mechanism, resistances of film mass transfer and pore diffusion are neglected. By substituting $1/R_{\text{chem}}$ into Eqn. (2.93) for $K(t)$, and combining with the expression for ξ_c in Eqn. (2.92), an expression for the transient is written as:

$$\frac{[CO_2]_E - [CO_2]_R}{[CO_2]_E - [CO_2]_I} = \frac{1}{1 + \frac{c_2}{L} k_c e^{-2t/\tau_{cb}}} \quad (2.94)$$

By applying the condition that $[CO_2]_R$ is equal to $[CO_2]_O$ at time zero, the resulting expression can be written:

$$\frac{\{[CO_2]_E - [CO_2]_O\} \{[CO_2]_R - [CO_2]_I\}}{\{[CO_2]_E - [CO_2]_R\} \{[CO_2]_O - [CO_2]_I\}} = e^{-t/\tau_c} \quad (2.95)$$

where $\tau_c = \tau_{cb}/2 = c_2/(S-1)c_{1c}$. This represents a case where the time constant is independent of r_p and k_c , even though the chemical reaction is the only mechanism considered other than bulk mass transfer.

If pore diffusion is the secondary mechanism, and a flat plate is considered, Eqn. (2.93) becomes:

$$\frac{[CO_2]_E - [CO_2]_R}{[CO_2]_E - [CO_2]_I} = \frac{1}{1 + \frac{c_2}{L^2} \frac{D_{ec}}{(1 - \xi_c)}} \quad (2.96)$$

Substitution of the dimensionless core radius from Eqn. (2.96), and use of the Taylor series approximation for ξ_c , results in:

$$\left(\frac{[CO_2]_E - [CO_2]_R}{[CO_2]_R - [CO_2]_I} \right) = \left(\frac{[CO_2]_R - [CO_2]_I}{[CO_2]_E - [CO_2]_I} \right)^{-1} = \frac{c_{1c} L^2}{c_2^2 D_{ec}} t = \frac{1}{\tau_{cbd}} t \quad (2.97)$$

where $\tau_{cbd} = 2\tau_{cd} = c_2^2 D_{ec} / c_{1c} L^2$.

From these cases it is seen that bulk mass transfer may affect the reaction rate, but its effect will depend upon the relative strengths of the other mechanisms. If calcination is strongly influenced chemical reaction, bulk mass transfer changes the time constant such that it is no longer dependent upon particle size or chemical reaction rate. For pore diffusion, it doubles the time constant and changes the order of the response.

2.5 Sulfation model

Sulfation theory

Limestones and dolomites are naturally occurring sedimentary rocks found throughout the world. These stones generally have their origin in shallow seas where biogenic calcium was deposited in layers over long periods of time. The age of a particular vein of limestone has some impact on its physical characteristics. In their examination of 23 varieties of limestone, Dam-Johansen and Ostergaard [35] were able to group limestones into three distinct categories. Limestones of young geologic age, which constituted the first category, exhibited an open, highly porous texture. Chalk, an example of this type of limestone, exhibits a high degree of purity.

Chalk was formed on the floors of broad shallow continental seas at the end of the Cretaceous geological period, which extended from 65 to 130 million years ago [36]. The second category consisted of limestones of an intermediate geological age that have coarse grains and less porosity. The old limestones of the final category are compact and have a non-porous texture.

In their study, Dam-Johansen and Ostergaard found that the porous limestones were much more reactive than the older compact limestones. Some of the older limestones they tested had slightly higher calcined surface areas than chalks, which exhibited higher reactivity [35]. This seems to indicate that pore size may be of greater significance in limestone sulfation than surface area.

Carbonate rocks commonly consist of three minerals: calcite, aragonite and dolomite. Calcite and aragonite are both forms of CaCO_3 , but they have different crystal structures and solubilities. Dolomite, $\text{CaMg}(\text{CO}_3)_2$, consists of calcium and magnesium in approximately equal proportions. Calcined dolomite usually retains porosity better than calcined calcite. Since SO_2 reacts only at the CaO sites and not at the MgO sites, the reaction is less inhibited by the large molar volume change associated with sulfation. Greater porosity in dolomite allows SO_2 to diffuse farther into the dolomite particle without plugging pores. Variations of the proportions of dolomite and calcite lead to a variety of carbonate rocks, such as dolomite limestone and calcitic dolomite [37].

Borgwardt and Harvey [38] performed analyses on a broad spectrum of carbonate rocks. SO_2 reactivity in the dolomites and calcites that they tested showed a strong dependence on surface area and pore sizes in the calcine. They tested magnesite, MgCO_3 , and found that it showed virtually no SO_2 reactivity, although it had a significantly greater calcined surface area and equivalent pore volume when compared to the calcines. Marble, which is metamorphic CaCO_3 , showed little reactivity due to a small calcine surface area. Aragonite had the lowest SO_2 reactivity of the eleven stones tested with the exceptions of magnesite and marble. Although aragonite had the largest mean pore diameter, it had the smallest calcined pore volume and surface area [38]. One conclusion from this work is that mean pore diameter, surface area, and

pore volume are all important parameters. A small value for any one of these parameters can cause reduced sorbent performance.

The chemical make-up of limestone also is a factor in its ability to react with SO_2 . Dolomites have been shown to allow more CaO to react because the magnesium content causes an increase in surface area. The CaO component in dolomite tends to crystallize independently from MgO during calcination. The small grain size of CaO then results in a large CaO surface area. Increased pore volume upon calcination compensates for the decrease in pore volume that occurs when CaO reacts to form CaSO_4 [38]. This increase in reactivity in dolomites and dolomitic limestones due to magnesium content was also found in the investigation by Mulligan *et al.* [39]. Carello and Vilela [40] studied five Brazilian limestone varieties and did not find that magnesium content aided in the sulfation process. Their tests differed from others in the literature in that they sulfated calcines in pure SO_2 rather than in a simulated combustion atmosphere.

In their study of thirteen limestones, Mulligan *et al.* [39] found that limestones with high silica content produce high surface area calcines, which in turn improves their sulfation efficiency. Dam-Johansen and Ostergaard [35] found that ferric oxide adversely affects sulfur dioxide capacity, but other researchers [41, 42] have found that in some cases ferric oxide content improves sorbent performance.

Complete utilization of CaO in the calcined limestone particle is usually not possible because of the buildup of CaSO_4 , which limits access to active sites. The molar volumes of CaCO_3 , CaO , and CaSO_4 are 36.9, 16.9 and 46.9 cm^3/mol , respectively [43]. This results in a theoretical maximum utilization of 69 % without growth of the particle, when starting with a non-porous particle. Actual conversions can be much less due to sintering during calcination and the plugging of pores by CaSO_4 . At normal FBC operating conditions the net sulfation reaction is commonly written as:

This reaction is generally considered to be first order with SO_2 and zeroth order with oxygen when O_2 is greatly in excess. At higher temperatures, the reverse reaction needs to be considered. Additionally the presence of CO and H_2O at the reaction site may promote reductive decomposition of CaSO_4 [23]. These reactions are significant at temperatures in excess of 1000°C . An optimum temperature of sulfur sorption exists in the range of $800 - 850^\circ\text{C}$. At temperatures below this range the calcination rate is reduced, which leads to a decrease in surface area for reaction. At temperatures above this range three phenomena contribute to a reduced conversion: more rapid plugging of pores caused by higher reaction rates, sintering of the CaO matrix, which reduces surface area, and participation of reverse and reductive decomposition reactions [39, 23, 28, 29].

Dam-Johansen and Ostergaard [44] present the sulfation reaction more generally as a reaction which produces calcium sulfite as an intermediary step:

The CaSO_3 then reacts to form CaSO_4 and calcium sulfide (CaS) depending upon the oxygen concentration by the net reactions:

Under reducing conditions such as are found in the dense phase of a circulating FBC, the presence of hydrogen sulfide, H_2S , may cause another reaction in which CaS is formed instead of CaSO_4

This reaction is significant for full scale FBC operations where combustion air is supplied in two

stages as a means of nitrogen oxide (NO_x) control. Higher sorbent utilizations can be achieved under these conditions, since the lower molar volume of CaS does not limit the extent of reaction, which is the result when CaSO_4 is the product. When exposed to oxidizing conditions CaS rapidly reacts to form CaSO_4 .

As in calcination, the reaction process takes place in several steps. The following mechanisms are generally thought to be important:

- 1) mass transfer from the particulate phase to the particle surface
- 2) diffusion through particle pores containing some level of CaSO_4 build up
- 3) diffusion at the grain level through a product layer, and
- 4) chemical reaction with CaO.

Unlike calcination, the sulfation reaction is assumed to be isothermal. Mass transfer from the bubble phase to the particulate phase is not usually considered, except that in some cases it is noted that depletion of SO_2 in the emulsion can cause a reduced reaction rate [23]. Another important difference between calcination and sulfation is that the diffusivity through the particle varies considerably during the process as CaSO_4 deposits in the pores.

Chemistry, pore diffusion, and product layer diffusion have all been proposed as rate limiting processes in the literature for different operating conditions, particle sizes, and reaction times. [23, 38, 39]. Borgwardt and Harvey [38] investigated eleven sorbents and found distinct behaviors that were dependent upon the mean pore size of the calcine. They measured an effectiveness factor, which was defined as the ratio of the reaction rate of a given particle size to that of small 0.096 mm particles of the same sorbent. For sorbents such as marbles and pure calcites, the mean pore diameter of around 0.075 μm caused rapid plugging of pores and low effectiveness factors. In these particles the reaction rate was proportional to $1/d_p^2$. For most of the limestones, which had calcine pore diameters ranging from 0.27 to 0.6 μm , the reaction rate was proportional to $1/d_p$ for particles larger than 150 μm . For smaller particles, the reaction rate was independent of particle size indicating a shift from diffusion to chemical reaction control. The marl and the aragonite they tested had pore diameters of 1.6 and 4.0 μm , respectively. These two

carbonate rocks showed no particle size dependence, indicating that they were controlled exclusively by chemistry control. For these particles, the large pores allowed the reaction to proceed evenly throughout the particle.

Other researchers have found that product layer diffusion is rate limiting [39, 45]. In this case the limiting step involves diffusion of reacting species through a product layer that surrounds CaO grains. The exact nature of this diffusion step is likely to be ionic diffusion, although this is not certain. Mulligan *et al.* [39] obtained a high activation energy for the reaction after an initial period in which the product layer was forming. This led them to conclude that the reaction was controlled by solid state diffusion with the diffusing species probably being Ca^{+2} and O^- ions. Bhatia and Perlmutter [45] similarly found a high activation energy for diffusion of 28.7 kcal/mol, which is in a range of values commonly found for ionic diffusion. However, they do recognize that several other plausible mechanisms could be involved. One such mechanism may be activated crack nucleation of the CaSO_4 layer, which would allow SO_2 and O_2 to diffuse to the unreacted CaO grain core.

Hsia *et al.* [46, 47] experimentally determined that ionic diffusion of Ca^{+2} and O^- is indeed the mechanism involved in product layer diffusion. In their first experiment they imbedded inert platinum markers between CaO and CaSO_4 and observed that the product layer thickens by an outward growth mode. In this analysis they observed SEM maps that show the product phase extending away from the platinum in the direction of the CaSO_4 [46]. In further work they confirmed this conclusion using an enriched sulfur isotope to mark the direction of the diffusion process [47].

Determination of the controlling process is crucial to understanding the sulfation reaction. It is clear that the large number of variables such as pore size, surface area, temperature, and particle size all play a role in determining the controlling reaction for a given type of limestone. In addition, the reaction may initially be controlled by one mechanism, such as chemistry control, and then for later times be controlled by another mechanism. For these reasons it is important to evaluate the reactions under realistic conditions. In order to understand the reaction in the course

of changing controlling mechanisms, it is necessary to find an appropriate model for the reaction.

The goal of this study is to use transient gas analysis as a tool in characterizing sorbents. The approach to this investigation begins with the development of a model that realistically represents the mechanisms of the reaction, and simulates the reaction as it occurs in the laboratory combustor. Simplifications to this model under the assumption of specific controlling mechanisms are developed. These simplified models will correspond directly with transient data if the assumed controlling mechanism is valid. Finally, particle analysis is conducted to give a physical interpretation to the transient gas analysis. Upon validation of the transient gas analysis methods, application to full-scale boilers is considered.

Modeling of sulfation

Many different models for sulfation have been proposed in the literature. The reaction is complex because it involves a 175% increase in molar volume while proceeding from CaO to CaSO₄. This increase in volume, along with the wide variety of pore structures found in sorbents, causes modeling of this reaction to be difficult. Many of the mechanistic models provide an accurate representation of the reaction. The focus of the present study, however, is to characterize sulfation by time constants with time series analytical methods employed in the study. To determine such time constants, simpler models are developed from ordinary differential equations.

Zheng *et al.* [48] developed a semi-empirical model that considers first-order reaction in a CSTR. A mass balance with first order reaction gives:

$$C_{A_0}Q = C_AQ + k_s C_A S \quad (2.103)$$

Where k_s is the reaction rate coefficient based on the particle external surface area, S . Zheng *et al.* observed that progressive pore blocking causes the rate of reaction to decrease exponentially with time. This is modeled by assuming that the particle external surface area decays

exponentially with time, taking on the form:

$$S = S_o e^{-k_d t} \quad (2.104)$$

where $S_o = 3m_{LS}/\rho_{LS}r_p$. In these equations, k_d is a deactivation rate constant, m_{LS} is the mass of the batch, Q is the flow rate through the combustor, ρ_{LS} is the limestone density, and r_p is the diameter of a spherical particle. For continuous addition of limestone and coal, the fractional reduction in steady state SO_2 emissions compared to expected emissions in the absence of sorbent, η_s , is computed by:

$$\eta_s = \frac{(C_{Ao} - C_A)}{C_{Ao}} = 1 - \frac{1}{1 + K\beta} \quad (2.105)$$

In equation (2.105), β is the calcium-to-sulfur molar ratio, and K depends on particle properties, reactor operating conditions, reaction rate constant (k_s), and deactivation rate constant (k_d).

For transient analysis with batch addition, this model can be expressed as:

$$\frac{C_A}{C_{Ao}} = \frac{1}{1 + \frac{k_s S}{Q}} = \frac{1}{1 + \frac{3m_{LS}k_s}{Q\rho_{LS}r_p} e^{-k_d t}} \quad (2.106)$$

The time dependence for this system is determined by the deactivation rate constant, k_d . This simple model would be attractive, except that preliminary experiments performed in this study did not yield the simple exponential relationship suggested by Eqn. (2.106).

In the present study, a grain model that described sulfation in terms of ordinary differential equations was first attempted. This model, developed by Christofides and Brown [49], considered film diffusion, pore diffusion through the particle, diffusion through a product layer at individual grains, and reaction at a shrinking grain core. These processes are depicted in Fig. 2.1.

In this model, pore diffusion is described by a decaying exponential with a time constant of τ_p for pore plugging. An effectiveness factor, ε_s , is defined to relate pore diffusion through the particles and product layer diffusion at the grains. In this way only the grain radius is a parameter and the radial location in the particle is not considered in the model. The model is described by four ordinary differential equations:

$$\frac{d[SO_2]_R}{dt} = \frac{Q}{V_b} \{[SO_2]_i - [SO_2]_R\} - h_s a_p \frac{N_p}{V_b} \{[SO_2]_R - [SO_2]_S\} \quad (2.107)$$

$$\frac{d[SO_2]_S}{dt} = \frac{h_s a_p N_p}{V_b} \{[SO_2]_R - [SO_2]_S\} - \varepsilon_s \frac{D_{pl} a_{gc} N_p}{t_{pl} V_b} \{[SO_2]_S - [SO_2]_{gc}\} \quad (2.108)$$

$$\frac{d[SO_2]_{gc}}{dt} = \varepsilon_s \frac{D_{pl} a_{gc} N_p}{t_{pl} V_b} \{[SO_2]_S - [SO_2]_C\} - \frac{k_s a_{gc} N_p}{V_b} [SO_2]_C \quad (2.109)$$

$$\frac{dr_{gc}}{dt} = - \frac{k_s M_{CaO}}{\rho_{CaO}} [SO_2]_C \quad (2.110)$$

Where the effectiveness factor is given by:

$$\varepsilon_s = \frac{3}{\phi_s} (\phi_s \coth \phi_s - 1) \quad (2.111)$$

In equation (2.111) ϕ_s is a Thiele modulus for sulfation, which is expressed by:

$$\phi_s = r_p \sqrt{\frac{D_{pl} \rho_{CaO} S_g}{t_{pl} D_{es_0} e^{-t/\tau_p}}} \quad (2.112)$$

Pore diffusivity decays exponentially with time according to the time constant, τ_p . As the pore diffusivity becomes smaller, the Thiele modulus becomes larger, and the reaction is controlled by

product layer diffusivity at the grain level. In this case the effectiveness factor approaches $3/\phi_s$.

An advantage of this initial approach to modeling was that time constants for different rate-limiting conditions could be derived by using quasi-equilibrium assumptions, and applied to experimental data. Unfortunately, this model did not always correlate well with lab scale experimental data. Part of the problem may have been that it did not include a mechanism for determining conversion to CaSO_4 or SO_2 concentration at a given radius within the particle. The grain core radius should be a function of the radial location within the particle. A more detailed analysis of this model is found in Christofides [23].

The current model employed in this study is a shrinking particle core model with an exponential decay of pore diffusivity. The model assumes reaction at particle core surfaces, which is common for reactions that are controlled by diffusion into the particle. It does not consider a mechanism at the grain level, i.e., product layer diffusion. Therefore, the model loses some of the detail of mechanistic models, but retains the simplicity of being solved by a series of ordinary differential equations:

$$\frac{d[\text{SO}_2]_R}{dt} = \frac{Q}{V_b} \{[\text{SO}_2]_I - [\text{SO}_2]_R\} - h_s a_p \frac{N_p}{V_b} \{[\text{SO}_2]_R - [\text{SO}_2]_S\} \quad (2.113)$$

$$\frac{d[\text{SO}_2]_S}{dt} = \frac{h_s a_p}{V_F} \{[\text{SO}_2]_R - [\text{SO}_2]_S\} - \frac{4\pi}{V_F} \frac{\delta_{es} e^{-t/\tau_p}}{\left(\frac{1}{r_{pc}} - \frac{1}{r_p}\right)} \{[\text{SO}_2]_S - [\text{SO}_2]_{SC}\} \quad (2.114)$$

$$\frac{d[\text{SO}_2]_{SC}}{dt} = \frac{4\pi}{V_L} \frac{\delta_{es} e^{-t/\tau_p}}{\frac{1}{r_{sc}} - \frac{1}{r_p}} \{[\text{SO}_2]_S - [\text{SO}_2]_{SC}\} - \frac{k_S a_{pc}}{V_L} [\text{SO}_2]_{SC} \quad (2.115)$$

$$\frac{dr_{sc}}{dt} = -\frac{k_S M_{\text{CaO}}}{\rho_{\text{CaO}}} [\text{SO}_2]_{SC} \quad (2.116)$$

As in calcination, a quasi-steady approximation is applied to this model and time derivatives of $[SO_2]$ are set equal to zero. The model then simplifies to one ordinary differential equation and one algebraic equation:

$$-\frac{dr_{sc}}{dt} = \frac{[SO_2]_I \frac{M_{CaO}}{f_{CaO} \rho_{LS}}}{\frac{3m_{LS}}{Q\rho_{LS}r_p} \frac{r_{sc}^2}{r_p^2} + \frac{1}{h_s} \frac{r_{sc}^2}{r_p^2} + \frac{(r_p - r_{sc})r_{sc}}{D_{es}e^{-t/\tau_p} r_p} + \frac{1}{k_s}} \quad (2.117)$$

$$\frac{[SO_2]_R}{[SO_2]_I} = \frac{1}{1 + \frac{3m_{LS}}{Q\rho_{LS}r_p} \left(\frac{1}{\frac{1}{h_s} + \frac{(r_p - r_{sc})r_p}{D_{es}e^{-t/\tau_p} r_{sc}} + \frac{1}{k_s} \frac{r_p^2}{r_{sc}^2}} \right)} \quad (2.118)$$

This model, like that for calcination, can be extended to non-spherical particles with a shape factor, S , and a characteristic length, L . With these modifications, and defining ξ_s equal to r_{sc}/r_p , Eqns. (2.117) and (2.118) become:

$$-\frac{d\xi_s}{dt} = \frac{[SO_2]_I \frac{M_{CaO}}{f_{CaO} \rho_{LS} L}}{\frac{Sm_{LS}}{Q\rho_{LS}L} \xi_s^{(S-1)} + \frac{1}{h_s} \xi_s^{(S-1)} + \frac{L(1-\xi_s)\xi_s^{(S-1)/2}}{D_{es}e^{-t/\tau_p}} + \frac{1}{k_s}} \quad (2.119)$$

$$\frac{[SO_2]_R}{[SO_2]_I} = \frac{1}{1 + \frac{Sm_{LS}}{Q\rho_{LS}L} \left(\frac{1}{\frac{1}{h_s} + \frac{L(1-\xi_s)}{D_{es}e^{-t/\tau_p} \xi_s^{(S-1)/2}} + \frac{1}{k_s \xi_s^{(S-1)}}} \right)} \quad (2.120)$$

If one of the resistances in Eqns (2.119) and (2.120) is considerably larger than the others,

then limiting behavior is observed. At time zero, the pore diffusion resistance is zero, since r_p and r_{sc} coincide. Accordingly, for early times in the transient, sulfation is controlled either by the chemical reaction or film diffusion. At later times the pore diffusion resistance becomes infinite and pore diffusion is rate-limiting. For cases where the film diffusion and chemical reaction resistances are small throughout the reaction, Eqn. (2.120) becomes:

$$\frac{[SO_2]_R}{[SO_2]_I} = \frac{1}{1 + \frac{3m_{LS}}{Q\rho_{LS}r_p} \left(\frac{r_{sc}D_{es}}{(r_p - r_{sc})r_p} \right) e^{-t/\tau_p}} \quad (2.121)$$

which is similar to the result derived by Zheng *et al.* [48], except the chemical reaction rate is replaced by a pore diffusion term.

Sulfation model simplification for limiting behavior

An objective of this investigation is to find time constants to characterize sorbent reactions analytically through time series or spectral methods. The shrinking core model with decaying diffusivity as shown in Eqns. (2.119) and (2.120) is useful in analyzing the transients, but comparison must be done numerically. The model can be simplified further by assuming rate-limiting mechanisms. To simplify the expressions, two constants are defined:

$c_1 = [SO_2]_I M_{CaO} / f_{CaO} \rho_{CaO}$, and $c_2 = Sm_{LS} / \rho_{LS} Q$. For the present discussion, analysis will be for spheres unless otherwise indicated.

Chemical reaction control

If chemical reaction is the controlling mechanism, the chemical reaction resistance term in Eqns. (2.119) and (2.120) is larger than the other resistances so that the equations may be rewritten:

$$-\frac{d\xi_s}{dt} = \frac{c_{1s}}{L} k_s \quad (2.122)$$

$$\frac{[SO_2]_R}{[SO_2]_I} = \frac{1}{1 + \frac{c_2}{L} k_s \xi_s^2} \quad (2.123)$$

Equation (2.122) can be integrated directly to yield:

$$\xi_s = 1 - \frac{c_{1s}}{L} k_s t \quad (2.124)$$

which is the first two terms of the Taylor series expansion for the exponential function.

Consequently, for short times ξ_s may be approximated by:

$$\xi_s = e^{-t / \tau_{sk}^*} \quad (2.125)$$

where $\tau_{sk}^* = L/k_s c_{1s}$. Substituting this result into Eqn. (2.123) and inverting the equation results in:

$$\frac{[SO_2]_I}{[SO_2]_R} - 1 = \frac{c_2}{L} k_s e^{-2t / \tau_{sk}^*} \quad (2.126)$$

Recognizing that $[SO_2]_R$ is equal to $[SO_2]_O$ at time zero, the equation takes on the form:

$$\frac{\frac{[SO_2]_I}{[SO_2]_R} - 1}{\frac{[SO_2]_I}{[SO_2]_O} - 1} = e^{-t / \tau_{sk}} \quad (2.127)$$

where $\tau_{sk} = \tau_{sk}^* / 2 = r_p / 2k_s c_{1s} = L / (S-1)k_s c_{1s}$.

The sulfation time constant, τ_s , can be determined graphically from the slope of a log-linear plot of Eqn. (2.127). If chemistry is rate limiting, τ_s will vary directly with particle size and inversely with the chemical reaction rate coefficient and inlet SO_2 concentration. A plot of $1/\tau_s$ versus $1/T$ will yield the true activation energy for chemistry reaction controlled sulfation. If particle shapes other than spheres are used, τ_s will be proportional to $\tau_{sk}/(S-1)$. For flat plates this results in an infinite value for τ_s , corresponding to a constant outlet concentration. For every shape, chemistry control results in an interface that recedes at a constant rate.

Film diffusion control

If sulfation is controlled by diffusion through the gas film surrounding the particle, the film diffusion resistances will be much larger than the other resistances. For the film diffusion control case, Eqns (2.119) and (2.120) become:

$$-\frac{d\xi_s}{dt} = \frac{c_{1s} h_s}{L \xi_s^2} \quad (2.128)$$

$$\frac{[\text{SO}_2]_R}{[\text{SO}_2]_I} = \frac{1}{1 + \frac{c_2}{L} h_s} \quad (2.129)$$

Integration of Eqn. (2.128) and application of the Taylor series expansion of the exponential function result in:

$$\xi_s = e^{-t/\tau_{sh}} \quad (2.130)$$

where $\tau_{sh} = L/h_s c_{1s}$. Equation (2.129) shows that the concentration transient is constant with time for film diffusion control. This response has not been observed in laboratory experiments nor in the literature. Although film diffusion may play a role in the sulfation process, it does not act as

the sole controlling mechanism.

Pore diffusion control

Up to this point the model under consideration has had an exponentially decaying pore diffusivity. To illustrate the effect of pore diffusion control, the sulfation mechanism will be examined first with a constant diffusivity, and then a decaying term will be incorporated. Analysis for pore-diffusion control and pore-plugging control is done for flat plates, utilizing the inherently simpler mathematics for this shape. Flat plate analysis is a particularly reasonable approach if pore-plugging occurs before a large shell of CaSO_4 builds up.

For pore diffusion control with an effective diffusivity which is constant with time and radius, Eqn. (2.129) becomes:

$$-\frac{d\xi_s}{dt} = \frac{D_{es} c_{1s}}{L^2(1-\xi_s)} \quad (2.131)$$

Integration of Eqn. (2.131) yields:

$$(1-\xi_s)^2 = \frac{2D_{es}c_{1s}}{L^2}t = t/t_s \quad (2.132)$$

where t_s , the time to completely sulfate the particle, is $L^2/(2D_{es}c_{1s})$. The expression for the dimensionless core radius is:

$$\xi_s = 1 - \sqrt{\frac{t}{t_s}} \quad (2.133)$$

The sulfation transient for pore diffusion limitation can be analyzed by writing Eqn. (2.120) for pore diffusion control:

$$\frac{[SO_2]_I}{[SO_2]_R} - 1 = \frac{c_2 D_{es}}{L^2 (1 - \xi_s)} \quad (2.134)$$

Inversion and substitution of Eqn. (2.133) into Eqn. (2.134) yields:

$$\left(\frac{[SO_2]_I}{[SO_2]_R} - 1 \right)^{-1} = \left(\frac{[SO_2]_I}{[SO_2]_I - [SO_2]_R} - 1 \right) = \frac{L^2}{c_2 D_{es}} \sqrt{t/t_s} = \sqrt{t/\tau_{sd}} \quad (2.135)$$

where $\tau_{sd} = c_2^2 D_{es} / 2c_{1s} L^2$. By making use of a Taylor series approximation, the linearized equation for short times is:

$$\left(\frac{[SO_2]_I}{[SO_2]_I - [SO_2]_R} \right) = 1 + \left(\frac{t}{\tau_{sd}} \right)^{1/2} = e^{\sqrt{t/\tau_{sd}}} \quad (2.136)$$

Inverting once more results in:

$$1 - \frac{[SO_2]_R}{[SO_2]_I} = e^{-\sqrt{t/\tau_{sd}}} \quad (2.137)$$

The sulfation time constant, τ_{sd} , can be determined from the reciprocal slope of a "log-squared"-linear plot:

$$\left\{ \ln \left(1 - \frac{[SO_2]_R}{[SO_2]_I} \right) \right\}^2 = \frac{1}{\tau_{sd}} t \quad (2.138)$$

Alternatively, Eqn. (2.135) results in a simple expression:

$$\left(\frac{[SO_2]_I}{[SO_2]_R} - 1 \right)^{-2} = \frac{1}{\tau_{sd}} t \quad (2.139)$$

which is valid for all times and can be plotted directly to fit a value of τ_{sd} .

Pore plugging control

The model described in Eqns. (2.119) and (2.120) incorporates an exponential decay in the effective diffusivity. Sulfation may be limited, not by the initial pore diffusion resistance, but by the effects of pore plugging. An exponential decay in diffusivity is used as an empirical model to describe pore plugging. Other investigators [50, 51] have used the local conversion at the grain or micro-grain level to drive the change in effective diffusivity. In this investigation, the pore-plugging time constant, τ_p , is an empirical parameter useful in assessing the rate-limiting mechanism of sulfation. For pore-plugging control of flat plates, Eqn. (2.119) can be written as:

$$-\frac{d\xi_s}{dt} = \frac{c_{ls} D_{es} e^{-t/\tau_p}}{L^2 (1 - \xi_s)} \quad (2.140)$$

Integration of Eqn. (2.140) yields:

$$(1 - \xi_s)^2 = \frac{\tau_p}{t_s} \left(1 - e^{-\frac{t}{\tau_p}} \right) \quad (2.141)$$

so that the dimensionless core radius is:

$$\xi = 1 - \sqrt{\frac{\tau_p}{t_s} \left(1 - e^{-\frac{t}{\tau_p}} \right)} \quad (2.142)$$

The significance of Eqn. (2.142) is that it predicts a final sulfation layer thickness. At late times, the thickness of the layer is $L\sqrt{\tau_p/t_s}$. Since the time for total sulfation, t_s , is a function of L^2 , the ultimate layer thickness for pore-plugging control is independent of particle size.

Analysis of the sulfation transient for pore plugging control can be made by assuming that pore-plugging is the limiting resistance in Eqn. (2.120). This results in the expression:

$$\frac{[SO_2]_I}{[SO_2]_R} - 1 = \frac{c_2 D_{es} e^{-\frac{t}{\tau_p}}}{L^2 (1 - \xi_s)} \quad (2.143)$$

Direct substitution of Eqn. (2.142) into Eqn. (2.143) gives:

$$\frac{[SO_2]_I}{[SO_2]_R} - 1 = \frac{c_2 D_{es} e^{-\frac{t}{\tau_p}}}{L^2 \left\{ 1 - \left[1 - \sqrt{\frac{\tau_p}{t_s}} \left(1 - e^{-\frac{t}{\tau_p}} \right) \right] \right\}} \quad (2.144)$$

For early times, the Taylor series expansion for e^{-t/τ_p} allows the simplification of Eqn. (2.144) to:

$$\frac{[SO_2]_I}{[SO_2]_R} - 1 = \frac{c_2 D_{es} e^{-\frac{t}{\tau_p}}}{L^2 \sqrt{\frac{t}{t_s}}} \quad (2.145)$$

At early times in the reaction, $\exp(-t/\tau_p)$ is close to unity and the equation then becomes the parabolic equation for pore diffusion control, Eqn. (2.139). At very late times in the reaction, the denominator of Eqn. (2.145) becomes a constant relative to the numerator. At these late times the transient approaches the background exponentially with the pore-plugging time constant.

Thus, at long times, a log-linear plot of Eqn. (2.145) will give the pore-plugging time constant.

The end of the transient presents some experimental difficulties, however. Small fluctuations are magnified on a log-linear plot as the background concentration is approached. Additionally, small changes in background concentration affect the analysis by changing the estimated value of $[\text{SO}_2]_i$. An alternative method is to measure τ_p early in the transient by plotting:

$$-\ln\left\{\left(\frac{[\text{SO}_2]_i}{[\text{SO}_2]_R} - 1\right)\sqrt{t}\right\} = \frac{1}{\tau_p}t - \ln\left\{\frac{c_2}{L} \sqrt{\frac{D_{es}}{2c_{1s}}}\right\} = \frac{1}{\tau_p}t - \ln\sqrt{\tau_{sd}} \quad (2.146)$$

which gives a line with a slope of $1/\tau_p$. The intercept of this line can be used to find the diffusivity time constant, τ_{sd} , and also the value of D_{es} .

Bulk mass transfer control

If bulk mass transfer is the controlling mechanism, the bed mixing resistance ($3m_{LS}/\rho_{LS}Qr_p$) is significantly larger than the other resistances. For this case Eqn. (2.119) can be written:

$$-\frac{d\xi_s}{dt} = \frac{c_{1s}}{c_2\xi_s^2} \quad (2.147)$$

Integrating and using the Taylor series expansion for the exponential function, Eqn. (2.147) becomes:

$$\xi_s = e^{-t/\tau_{sb}} \quad (2.148)$$

where $\tau_{sb} = c_2/c_{1s}$. Simplification of Eqn. (2.120) for film diffusion control results in:

$$\frac{[SO_2]_R}{[SO_2]_I} = \frac{1}{1 + \frac{c_2}{L} K(t)} \quad (2.149)$$

In Eqn. (2.149), $K(t)$ is the overall reaction coefficient from the other resistances. Since the chemical and diffusion resistance terms are time dependent, $K(t)$ is written as a function of time. This allows for consideration of two cases in which bulk mass transfer is the primary controlling mechanism and either chemical reaction resistance or pore diffusion resistance is the secondary controlling mechanism.

For the case in which chemical reaction is the secondary mechanism, resistances of film mass transfer and pore diffusion are neglected. By substituting $1/R_{chem}$ into Eqn. (2.149) for $K(t)$, and combining with the expression for ξ in Eqn. (2.148), an expression for the transient is written as;

$$\frac{[SO_2]_R}{[SO_2]_I} = \frac{1}{1 + \frac{c_2}{L} k e^{-2t/\tau_{sb}}} \quad (2.150)$$

By applying the condition that $[SO_2]_R$ is equal to $[SO_2]_O$ at time zero, the resulting expression can be written:

$$\frac{\frac{[SO_2]_I}{[SO_2]_O} - 1}{\frac{[SO_2]_I}{[SO_2]_O} - 1} = e^{-t/\tau_s} \quad (2.151)$$

where $\tau_s = \tau_{sb}/2 = c_2/(S-1)c_{1s}$. This represents a case where the time constant is independent of r_p and k_s , even though the chemical reaction is the only mechanism considered other than bulk mass transfer.

If pore diffusion is the secondary mechanism, and a flat plate is considered, Eqn. (2.149)

becomes,

$$\frac{[SO_2]_R}{[SO_2]_I} = \frac{1}{1 + \frac{c_2 D_{es}}{L^2 (1 - \xi_s)}} \quad (2.152)$$

Substitution of the dimensionless core radius from Eqn. (2.148) results in:

$$\left(\frac{[SO_2]_I}{[SO_2]_R} - 1 \right)^{-1} = \frac{c_1 S L^2 t}{c_2^2 D_{es}} \quad (2.153)$$

For early times, the equation may be written as:

$$-\ln \left(\frac{[SO_2]_I - [SO_2]_R}{[SO_2]_I - [SO_2]_O} \right) = \frac{1}{2\tau_{sd}} t \quad (2.154)$$

If a decaying value of pore diffusivity is considered, the equation becomes:

$$\left(\frac{[SO_2]_I}{[SO_2]_R} - 1 \right) = \frac{c_2 D_{es} e^{-t/\tau_p}}{L^2 (1 - e^{-t/\tau_{sb}})} \quad (2.155)$$

which for early times reduces to the pore diffusion case of Eqn. (2.154). For later times the response approaches background at the pore-plugging time constant.

As in calcination, bulk mass transfer may affect the reaction, but its effect will depend upon the relative strengths of the other mechanisms. For sulfation ordinarily controlled by chemical reaction, bulk mass transfer changes the time constant such that it is no longer dependent upon particle size or chemical reaction rate. For pore diffusion, it doubles the sulfation time constant, and changes the order of the response. For pore plugging, the difference is only in

the initial part of the transient. At early times the transient is described by the linear pore diffusion response of Eqn. (2.153).

2.6 Spectral analysis

The investigation of the dynamic response of a system can be conveniently tested with spectral analysis [52]. Spectral analysis is frequently used in designing and analyzing automatic control systems and has potential as a powerful tool in evaluating fundamental physical processes occurring in a system, including coal combustion in a boiler.

Characterization of fuels in a fluidized bed boiler by this method is complicated as it depends on the ability to approximate specific, complex physical processes with low-order, linear models and on the sensitivity of the signal processing equipment algorithms and the data analysis. However, systems operating close to steady-state, for which only a single input variable is perturbed, can often be represented by a linear, ordinary differential equation of low order [53].

The theory that spectral analysis of CO_2 and CO concentrations at the outlet of a combustor could be used to evaluate the devolatilization and char burnout times was tested. Characteristic times were compared to combustion parameters employed in a computer model of coal combustion to determine if the characteristic times were, in fact, the devolatilization and char burnout times.

Signal Identification

Graupe [54] states that the characteristics of a system can be identified using Fourier transform techniques by measuring the response of the system to a specific input. He lists three types of inputs used in system identification: step, sinusoidal, and impulse.

The system response $y(t)$ of a dynamic system $g(t)$ to an impulse input function $u(t)$, can be represented by the block diagram of Fig. 2.2.

The transfer function of a first order linear process is given by Eqn. (2.156) [52, 54, 55]:

$$G(i\omega) = \frac{K}{\tau i\omega + 1} \quad (2.156)$$

where τ is the characteristic time of the system and K is the system gain. Consequently, the system response to an impulse input is [52, 54]:

$$g(t) = \mathcal{F}^{-1}G(i\omega) = \frac{K}{\tau} e^{-t/\tau} \quad (2.157)$$

The transfer function and impulse response function of a linear time-invariant system both contain the same information about system dynamics [55]. The transfer function of a system may be derived by applying the Fourier transformation to the response to an impulse input [54]. It is possible to obtain complete information about the dynamic characteristics of the system by exciting it and measuring the response [54].

The Fourier transform of the impulse response $y(t)$ is given by:

$$Y(j\omega) = G(j\omega) \cdot U(j\omega) = G(j\omega) \cdot 1 \quad (2.158)$$

where $Y(j\omega)$, $G(j\omega)$, and $U(j\omega)$ are the Fourier transforms of $y(t)$, $g(t)$, and $u(t)$ respectively, and the input function is an impulse. If $Y(j\omega)$ is plotted versus frequency ω , the frequency response $G(j\omega)$ of the system is obtained [54]. $G(s)$ may now be derived from $G(j\omega)$ by employing Bode diagram techniques. On a Bode diagram, $20\log_{10}|G(j\omega)|$ vs. $\log_{10}(\omega)$, the asymptote is horizontal for $\omega < 1/\tau$, and has a slope of -20db/decade at $\omega > 1/\tau$ [54, 55].

Junk [56] applied control theory techniques to the study of coal combustion and developed a transfer function (Eqn. (2.159))

$$Y(s) = \frac{b_1 s + b_0}{s^2 + a_1 s + a_0} \quad (2.159)$$

to describe the impulse response of the combustion process for large coal particles (about 5 mm diameter). This transfer function represents the Laplace transform of two concurrent first order processes (Eqn. (2.160)) with A and B being process

$$y(t) = A \exp(-t / \tau_v) + B \exp(-t / \tau_c) \quad (2.160)$$

gains and τ_v and τ_c characteristic times, with τ_v less than τ_c . In Eqn. (2.160) the coefficients a_i and b_i are:

$$a_0 = \tau_v \tau_c \quad (2.161)$$

$$a_1 = \tau_v + \tau_c \quad (2.162)$$

$$b_0 = A \tau_v + B \tau_c \quad (2.163)$$

$$b_1 = A + B \quad (2.164)$$

For small particles the transfer function Junk [56] obtained (Eqn. (2.165)) contained second order numerator dynamics :

$$Y(s) = \frac{b_2 s^2 + b_1 s + b_0}{s^3 + a_2 s^2 + a_1 s + a_0} \quad (2.165)$$

and third order denominator dynamics because it modeled the inflection contained in the char burnout at longer times due to the end of burning of the smallest particles in the batch prior to the other particles.

3. EXPERIMENTAL APPARATUS AND METHODS

3.1 Laboratory fluidized reactor

A diagram of the laboratory scale bubbling fluidized bed combustor (FBC) is shown in Fig. 3.1. The FBC has a diameter of 20 cm. Five liters of sand with particle diameters ranging from 0.6 to 1.2 mm were used to make a bed approximately 15 cm in height. For coal analysis the sand was river bed sand obtained from a local quarry. For sulfation experiments the sand was a 99% pure silica sand obtained from the Badger Mining Co. of Fairwater, Wisconsin. A mixture of fuel and air fluidized the sand after passing through a diffuser plate consisting of 166 holes of 2.4 mm diameter spaced 1.4 cm apart in a square grid.

The primary fuel was methane from the building natural gas lines, but propane from 20 pound cylinders was used initially and during some of the later sorbent testing. A model 102 Accurate auger feeder was also used to feed modulated flows of coal into the combustor. The feeder was computer controlled and had a ramp time of 0.25 s. Combustion air was provided from the building compressed air lines. Pressure upstream of the air flow meter was regulated to 60 psia for calibration of the flow meter and during operation. Air flow was measured via a Shaevitz p3061 linear-variable-differential transformer (LVDT) pressure transducer. Compensation for the zero shift on the pressure transducer was available within the data acquisition code. Air flow was controlled either by a manual valve or by a pneumatically-controlled Fisher Design air flow valve with a Fisher Type 513 R reversible diaphragm actuator receiving control signals from the data acquisition system. Calibration of the air flow meter was done using a standard wet test flow meter manufactured by the American Meter Co. of New York. The error for this calibration was approximately 5% of full scale.

Ignition of the air and natural gas was achieved above the bed via two electrodes connected to a 10 kV transformer. Temperatures were measured by type K thermocouple probes in the center and side of the bed. Thermocouples also were used to record temperatures in the lower and upper sections of the freeboard. The thermocouples provided an accuracy of $\pm 6^\circ \text{C}$.

Exiting combustion gases passed through a cyclone separator where elutriated particles were removed.

Batch tests were conducted by heating the bed to the desired temperature and then adjusting fuel and air flow to obtain the flow rate desired. For coal tests the standard baseline conditions were a bed temperature of 850°C and a superficial velocity of 1 m/s. At these conditions using propane the oxygen level measured in the analyzer was 6-7% and the background CO₂ level measured by its analyzer was 7-8%. When using methane the background oxygen concentration was 4-5%. Instrument concentrations were compensated for the water vapor removed during the sampling process when determining sorbent conversions. For sorbent testing pure SO₂ was injected to the air upstream of the distributor plenum via a small needle valve to control SO₂ background levels to within ± 10 ppm of the desired value as read on the data acquisition computer. Fuel, air, and SO₂ flows were then left to steady for 30 minutes to an hour prior to starting the first test due to slow transients in temperature and SO₂ concentration. A wide variety of conditions were used for these tests but the standard condition was a bed temperature of 850°C, a superficial velocity of 1 m/s, and a background SO₂ instrument concentration of 1500 ppm. Nitrogen and CO₂ were also added to the air line to test at varied oxygen and CO₂ concentrations.

3.2 Laboratory instrumentation

The gas was sampled at two locations and drawn through one of two sample lines by a common double diaphragm vacuum pump. One sample location was in the exhaust line after the cyclone separator. This sample line was used when coal combustion was the means of steady-state combustion. A condensing tar trap was used in this situation to remove tars from the gas before it contacted the sample cart equipment. This sample gas passed through a Balston 30/12 microfibre filter to remove small particulates and a Perma-Pure F-275-EG acid mist filter. Water vapor was removed from the sample gas by a Perma-Pure PD625-24APS membrane dryer, which consisted of fifty 0.5 mm diameter organic semi-permeable membrane tubes. Dry air from a Perma-Pure

HD202-b heatless zeolite dryer passed over the outside of the membranes inside the stainless steel tube. Moisture from the gas flowed through the semi-permeable tubes into the dry purge air due to water vapor partial pressure gradient.

The second sample line was the same as the first except that it drew sample gas from the upper freeboard of the combustor. It used a smaller Balston 9556 filter and a smaller Perma-pure model FF-250-56-2.5G acid mist filter. The Perma-Pure PD 1000 membrane dryer used had two hundred 0.5 mm diameter membranes for increased moisture removal. This sample line was used for long-term combustion of methane or propane due to the higher water vapor content in the product gases.

Both sample lines were heated electrically with heat tapes to maintain combustion gases well above local dew point temperatures. The sample system had type K thermocouples that were connected to the data acquisition system to monitor sample system component temperatures. The pump and heat tapes were programmed to shut down if temperatures at the Perma-pure or acid mist filter exceeded 93.3°C in order to protect the Perma-pure gas dryer elements.

The gas was directed from the vacuum pump to five gas analysis instruments. Measurements for CO₂, CO, SO₂, and NO_x were made on non-dispersive infrared (NDIR) instruments. The oxygen instrument was a paramagnetic instrument. Instruments were calibrated using certified blend gases obtained from Air Products, Inc. of Allentown, PA. These gases were certified to be within $\pm 2\%$ of the calibration value. Analyzer drifts and calibration gas concentrations are given in Table 3.1.

Two methods were used for drawing calibration gases. In the first method samples were drawn from the calibration gas cylinders via Tygon tubing connected from the cylinder regulator valves to the sample tubing line at the tar trap connection. A plastic bag was placed in series with the Tygon tubing to ensure that the samples were being drawn at approximately atmospheric pressure. In the second method Tygon tubing was run from the cylinder regulator valves to a hose barb at the start of the sample line into the gas analyzers. Cylinder regulators were adjusted to ensure that the flow rate into the gas analysis instruments was the same as when the system was

drawing sample gases during normal operation. It was assumed that equal flows into the instruments resulted in equal pressure in the instrument. The second method also had the advantage that manifold step tests could be performed with instantaneous switching of sample gases through an installed valve.

Instrument time constants for the analyzers were determined by performing step tests of the calibration gas and nitrogen. Gas flow into the instruments was controlled by flow meters to the recommended rates of 1.0 l/min for the CO₂, CO, SO₂, and NO_x instruments, and 0.5 l/min for the O₂ instrument. An increased flow rate of 3 l/min was used in later experiments for the SO₂ instrument to improve the instrument time constant. Time constants for CO₂, CO, and O₂ were matched to an exponential step change; e.g. for a step decrease:

$$C_A = C_{A_{\max}} e^{-t/\tau_i} \quad (3.1)$$

For CO and CO₂ the time constant, τ_i , was roughly 2 seconds, while for O₂ it was around 10 seconds.

The step change for SO₂ was 2 seconds after the flow rate was changed to 3 l/min. For most of the sorbent data, SO₂ instrument flow was the recommended 1 l/min. The time constant under this condition was best represented by the following expression. with time units of seconds:

$$\frac{[SO_2]}{[SO_2]} = .96e^{-t/6.5} + .04e^{-t/200} \quad (3.2)$$

Gas samples were also taken using the Nicolet (FTIR) analyzer prior to its installation at the ISU power plant. This system is discussed in section 3.3.

The data acquisition system consists of an HP Vectra 386 SX-16 computer configured with a Metrabyte 8 channel type DAS-8 A/D converter. Temperatures, gas concentrations, air flow, and bed differential pressure are monitored by the system. The type K thermocouples are

connected to two Metrabyte Model EXP-16 sub-multiplexer boards provided with a cold junction compensation. These signals are amplified to provide a 0-5 V DC signal to the DAS-8 converter. The DAS-8 also receives 0-5 V DC signals directly from the gas analyzers and from the air flow transducer. Control functions such as air flow and feed flow control, and automatic shutdown of gas analysis equipment are used as needed. The operating code is written in QuickBASIC 7 and converted into executable files. Data was recorded at a rate appropriate to the transient being measured, usually 5 data points per second. The maximum data rate was 7 data points per second.

The data acquisition program was initiated prior to starting the test. At least 30 seconds of data was recorded to verify that the background was steady. For sulfation tests 2 minutes of data were recorded prior to batching in the limestone. The samples were weighed using a Fisher Scientific Model XT-660-KS balance which has a range of 0-660 g and a sensitivity of 0.01 g. For coal tests the standard sample mass was 5 g. A 20 g or 30 g sample was typically used for sorbent tests, but other batch sizes were used when samples were to be extracted from the bed in the middle of the test, or for extremely small or large particle sizes. The sample was placed in the batch addition port with the ball valve shut. To initiate the transient, the ball valve was opened to let the sample fall into the bed. When small particles of limestone were used the fly ash collection jar below the cyclone was cleaned prior to the transient and removed ten minutes into the transient to find the approximate mass of elutriated limestone. The test was continued until the transient returned to the background concentration of SO_2 . During this time no adjustments were made to fuel, oxygen, or SO_2 flows into the reactor.

Analysis methods

After the bed was heated to 1116 K for coal characterization tests, the air flow was adjusted to obtain 6-7% oxygen in the exhaust gas. Perturbation in the steady-state CO_2 concentration was produced by batching small quantities, typically 5 g samples, of single-sized

coal particles into the bed. Gas concentrations as well as air flow and temperature were recorded until the CO_2 and O_2 concentrations returned to within 1% of their original steady state values.

One approach to analyzing char combustion from CO_2 profiles substitutes Eqn. (2.22) into Eqn. (2.17), linearizes the resulting expression for CO_2 with respect to time, and obtains characteristic char burnout times from the CO_2 profile in a manner similar to that used for devolatilization analysis. This approach was successfully employed in some of these experiments. However, this direct approach requires the use of relatively small coal samples to assure that the interphase mass transfer contribution to the characteristic char burning time is small compared to other contributions; otherwise, the analysis becomes complicated. An alternative analytical procedure that requires no special consideration of interphase mass transfer was found to be preferable. Furthermore, this alternative procedure, by integrating the CO_2 profile, reduces the influence of noise on signal analysis.

In this alternative approach, the decrease in particle diameter is calculated by assuming spherical particles burning as shrinking (constant density) cores:

$$\frac{d(t)}{d_i} = \left(\frac{m(t)}{m_i} \right)^{1/3} \quad (3.3)$$

where $m(t)$ is the mass of char carbon remaining in the bed at time t and m_i is the initial mass of carbon in the char. The quantity m_i is calculated by subtracting the cumulative mass of volatile carbon lost during devolatilization (as given by Eqn. (2.12) from the mass of elemental carbon in the sample of coal batched to the combustor):

$$m_i = (\% \text{ carbon}) \times m_{\text{coal}} - QM_c \int_0^{\infty} \{ [\text{CO}_2]_i - [\text{CO}_2]_f \} e^{-t/\tau_v} dt \quad (3.4)$$

The quantity $m(t)$ is found by subtracting the cumulative mass of carbon lost during char combustion from the initial mass of carbon in the char:

$$\frac{m(t)}{m_i} = 1 - \frac{QM_c}{m_i} \int_{t=0}^t \left\{ [CO_2]_R - ([CO_2]_i - [CO_2]_f) e^{-t/\tau_v} \right\} dt \quad (3.5)$$

According to Eqns. (2.24) and (2.27) and for times $3\tau_v < t < \tau_c$, a plot of $\ln(d(t)/d_i) = \ln(m(t)/m_i)^{1/3}$ vs. time is a straight line with negative reciprocal slope equal to τ_c .

This analytical procedure applied to experimental data is illustrated in Fig. 3.2, which is a typical CO_2 trace produced for a 5 g sample of 3.3 mm-diameter coal particles batched to the preheated fluidized bed. The trace peaks sharply, as devolatilization and char burning begin, drops rapidly as volatiles are exhausted, and then gradually declines as char is slowly consumed.

According to Eqn. (2.12), the characteristic devolatilization time τ_v , can be determined from the slope of the CO_2 trace immediately after peak concentration. The parameters $[CO_2]_f$ and $[CO_2]_i$ are determined by drawing asymptotic lines along the "devolatilization" and "char-burning" sections of the CO_2 trace, respectively, as illustrated in Fig. 3.2.

Typical CO_2 and SO_2 profiles from limestone tests are shown in Figs. 3.3 & 3.4. The background concentration was subtracted from the CO_2 profile. These profiles were used to find time constants for calcination and sulfation, and to determine extents of calcination and sulfation.

Figure 3.3 shows the change in % CO_2 during a test of 0.925 mm Gilmore City formation limestone at a temperature of 1123 K and a superficial velocity of 1.1 m/s. The profile shows an initial rise, the slope of which corresponds to sampling system delay time. The CO_2 concentration then decays roughly exponentially back to its background value. This second part of the transient is non-dimensionalized according to the equation

$$\frac{[CO_2]_R - [CO_2]_i}{[CO_2]_o - [CO_2]_i} = \exp\left(-\frac{t}{\tau_c}\right) \quad (3.6)$$

where $[\text{CO}_2]_0$ can be taken to be a point on the curve shortly after the peak. A semi-log plot of the transient after this point will give a straight line the inverse negative slope of which is the calcination time constant, τ_c .

In a similar fashion, τ_s can be determined for the sulfation transient. For short times and chemistry limited sulfation the SO_2 concentration can be expressed as

$$\frac{[\text{SO}_2]_R - [\text{SO}_2]_i}{[\text{SO}_2]_0 - [\text{SO}_2]_i} = \exp\left(-\frac{t}{\tau_s}\right). \quad (3.7)$$

More generally, the sulfation time constant is computed by:

$$\frac{\frac{[\text{SO}_2]_i}{[\text{SO}_2]_0} - 1}{\frac{[\text{SO}_2]_R}{[\text{SO}_2]_0} - 1} = \exp\left(-\frac{t}{\tau_s}\right). \quad (3.8)$$

A semi-log plot of the transient should then give a straight line the inverse negative slope of which is the sulfation time constant, τ_s . Alternative analysis can be done by fitting a series of these curves to the shrinking particle core model described in chapter 2 to determine particle parameters.

Estimates of extents of calcination and sulfation were done by numerically integrating the CO_2 profile and the difference between the SO_2 profile and the background SO_2 concentration. These integrals were multiplied by the volumetric flow rate through the combustor and divided by the theoretical mass of CO_2 and SO_2 released to give the extents of reaction. The resulting expressions for the extent of calcination is

$$\text{Extent of calcination} = X_c = \frac{Q \int_0^{\infty} \{[\text{CO}_2]_R - [\text{CO}_2]_i\} dt}{\frac{f_{\text{CaCO}_3} m_{\text{LS}}}{M_{\text{CaCO}_3}}}, \quad (3.9)$$

where $[\text{CO}_2]_R$ and $[\text{CO}_2]_i$ have dimensions of mol/volume, rather than mole fraction as is measured. The expression for extent of sulfation, which is also referred to as calcium utilization, is:

$$\text{Extent of sulfation} = X_s = \frac{Q \int_0^{\infty} \{[\text{SO}_2]_i - [\text{SO}_2]_R\} dt}{\frac{f_{\text{CaCO}_3} m_{\text{LS}}}{M_{\text{CaCO}_3}}}, \quad (3.10)$$

where $[\text{SO}_2]_i$ and $[\text{SO}_2]_R$ have dimensions of mol/volume, rather than the measured quantity of parts per million (ppm).

The change in volume between product and reactant gases is considered when computing the volumetric flow rate. For conversion results, compensation for water vapor removed in the perma-pure dryer is considered when determining the concentration values. It is assumed that 100% of the water vapor resulting from complete combustion is removed. Complete combustion stoichiometry is determined from the baseline CO_2 concentration prior to the transient. Results in the figures in this report show the CO_2 and SO_2 concentrations as measured by the instruments, without compensation for water vapor removal.

Samples of bed material were also withdrawn from the combustor for particle analysis. A sample extractor was made to pull out hot bed samples through the batch addition ball valve. This was done to compare transient gas analysis results to measurements made on the particles. Extracted samples were prepared by sealing them in an epoxy ring and then polishing them to provide a nearly cross-sectional view.

Samples were analyzed on a Hitachi model S-2460N Scanning Electron Microscope (SEM). This environmental SEM produced particle concentration maps which were used to evaluate the location of calcined and sulfated regions in the limestone particles. Microprobe line

scanning was also done using this instrument to measure sulfation layer thickness and concentration gradients.

Sulfated particles were made into thin sections for transmitted-light microscopy. This analysis provided an indication of particle grain size. Chemical analyses were performed on limestone and sulfated samples for comparison of actual conversion to that determined from transient gas analysis.

3.3 Circulating fluidized bed boiler

The number 2 circulating fluidized bed boiler at the Iowa State University power plant was instrumented to conduct industrial-scale boiler experiments. Figure 3.5 is a schematic of the boiler. The boiler is one of two Ahlstrom Pyropower, Inc. boilers installed at the power plant. At full load each of the two CFB boilers is rated at 77110.7 kg/hr (170,000 lb/hr) steam flow, 2895.5 kPa (420 psig), 399°C (750°F), 11,339.8 kg/hr (25,000 lb/hr coal flow rate), and 3,660.5 kg/hr (8,070 lb/hr) limestone flow rate. The bed material is limestone and ash, no sand is used. Normal operating condition is about 60% full load.

Coal is fed into the boiler at two points on opposite sides of the boiler combustion chamber. Mechanical drag conveyors transport the coal from the coal silos to feed pipes which enter the boilers. One point enters the loop seal about 3.05 m from the boiler, the other through a dedicated coal feed point on the opposite side. Both feed points have centerlines about 1.52 m above the nozzles. The two pneumatic limestone feed lines merge with the coal feed lines, and the coal and limestone are fed together. Coal feed rate varied from 5778.8 to 8337 kg/hr (12,740 to 18,380 lb/hr), while total air flow varied from 61,974.3 kg/hr (136,630 lb/hr) to 86,182.5 kg/hr (191,000 lb/hr).

The coal batch is introduced into the boiler through a hopper (Fig. 3.6) installed on the outlet end of the coal drag conveyor which dumps into the lower part of the bed opposite the loop seal. The hopper was custom designed to fit the existing coal drag conveyor and dump a batch of coal as fast as the valve could be opened. The hopper is an inverted, truncated conical cylinder on

top of a Zurick, Inc. 20.3 cm diameter slide gate valve. The valve has a manual operating mechanism which permits the valve to be opened in less than two seconds. Ducting below the valve directs the coal into the coal feed pipe below the conveyor in such a manner that it is not impeded by the chain of the drag conveyor. Experiments confirmed the coal was dumped as fast as the valve was opened, simulating an impulse input. The hopper was sized to hold up to 13.6 kg (30 lb) of coal, but all tests were performed with 10.9 to 12.7 kg (24 to 28 pounds) of coal, depending on size. The coal was weighed with a Hanson dairy scale, accurate to within 0.11 kg (1/4 pound).

Staged combustion is used in the boilers. Primary air is used in the nozzles and to fluidize the coal feed. Secondary air enters through 4 inlet pipes (two on each side) about 2.74 m above the nozzles, and is also used for the limestone pneumatic feed. The primary to secondary air ratio varied from 1.04 to 1.58. Figure 3.7 shows how the primary to secondary air ratios and total air flow to coal flow ratio varied with total coal feed rate. The general trend is for both ratios to decrease with increased coal feed rate. Coal and air rates were set by the boiler control system in response to system requirements during normal operation. The secondary air flow rate was set at least in part to control bed temperature. Values given were recorded as conditions existing at the time of testing.

The stoichiometric molar air to fuel ratio for the Illinois washed coal was calculated as 3.77. The average molar primary air flow to average fuel feed rate ratio was 3.37, with a low of 3.08 and high of 3.46. Thus, at least initially, the combustion process took place in a condition of slightly less than stoichiometric air flow. The percent change from low to average was 17%, which is significant and could impact the combustion process of the coal batched into the part of the bed below the secondary air inlet. Devolatilization and char time constants were compared to total air flow and coal feed rate for each test. No direct correlation between air or coal feed rate and time constant could be identified for each size coal. Although one particle size did indicate that time constants were proportional to air or coal feed rates, the trend for another size was inversely proportional. In yet other cases, the relations were totally random. While varying air

flow and coal feed rates may influence time constants, there is inadequate data in this work to support any definitive conclusions.

During these tests the boiler was fired with either Illinois washed coal or Kentucky coal, depending on availability.

3.4 Boiler instrumentation

A Fourier Transform Infrared (FTIR) spectrometer was chosen to analyze the gaseous products of combustion in the CFB boiler due to its ability to simultaneously identify and quantify multiple gases. The FTIR system (Fig. 3.8) includes a Nicolet Instrument Systems, Inc. Magna 550 FTIR with mercury cadmium telluride (MCT) detector and Infrared Analysis, Inc. model G-2-4-H-BA-Au 20 pass gas cell with 1.7 m pathlength. The volume of this cell is 275 ml, permitting rapid gas exchange and the detection of fast gas transients. However, since detection sensitivity is dependent on pathlength, the relatively short pathlength (compared to 10-20 m used in most gas analysis systems) has reduced sensitivity. For example, this cell lacks adequate sensitivity to detect 150 ppm of HCl, so this gas was not detected. This was a compromise made in order to detect rapid gas transients during devolatilization.

The FTIR runs Nicolet OMNIC software with series collect option for data collection and analysis. Nicolet Quantir software was used to develop the quantification methods.

A sample collection probe (Fig. 3.9) was inserted in an 8.89 cm dia. port installed in the hot cyclone outlet duct. The probe was a 1.22 m long 1.27 cm dia. 316 stainless steel tube surrounded by a 1.588 cm dia. 316 stainless steel pipe for rigidity and erosion protection. The tube and pipe were welded to a 15.24 cm dia. standard flange bolted to the port. The end of the probe was about a third of the way across the cyclone outlet duct and 30.48 cm from the top.

The sample tubing from the probe to the FTIR gas cell is 0.952 cm dia. stainless steel. In-line are a Balston model 30/12 in-line filter with DH element (F1), and two Balston 95S6 miniature T-type filter housings in series, the first with a DH element (F2) and the second with a BH element (F3). The DH elements are rated to remove 93% of 0.1 μm particles and the BH

element removes 99.99% of 0.1 μm particles. The filters remove flyash in the sample gas to protect the cell optics and prevent infrared absorption by the flyash particles. Also in-line is a Perma-Pure model PD-1000-48SS membrane air dryer to remove water vapor from the gas sample. The membrane dryer was used rather than condensing out the water vapor to prevent removal of SO_2 with the water.

A heating unit around the gas cell is controlled by a Barnant model 621-8600 temperature controller with type J thermocouple and maintains temperature at $82.2^\circ\text{C} \pm 0.5^\circ$. A needle valve on the vacuum pump inlet is manually adjusted to maintain cell pressure at 600 mm Hg ± 6 mm. The FTIR optical bench, computer, pressure controller, and temperature controllers are housed in a NEMA-12 cabinet with 5000 BTU air conditioning system to maintain temperature about 21°C and provide a dust free environment.

The gas sample is drawn through the sampling system by a Thomas model 2737-CM vacuum pump rated at $1.416 \times 10^{-3} \text{ m}^3/\text{sec}$ (3 scfm) at 10" Hg. A Purimetrix model KLDW purge air generator supplies dry, oil-free purge air to the bench to protect the hygroscopic optics, background gas to the cell in lieu of nitrogen due to ready availability, and dry air for the Perma-Pure membrane air dryer at the power plant. The purge air generator takes shop air at 786 kPa (100 psig) nominal and less than 37.8°C and produces $1.416 \times 10^{-3} \text{ m}^3/\text{sec}$ (3 scfm) dry air at -73.3°C dew point and less than 20 ppm CO_2 .

Gas concentrations were recorded on an Intel 80486 DXII/66 microcomputer operating with the FTIR optical bench. The computer is configured with 8 MB of RAM memory, an SVGA monitor, a 420 MB hard drive, and a Colorado Jumbo 250 tape backup system. The interface to the FTIR bench was through a Nicolet provided bench driver card.

A direct relation exists between number of scans averaged into one spectrum, the resolution, and the time interval between spectra. The higher the resolution, or the more scans recorded, the greater the time interval between spectra. Resolution was set to 2 cm^{-1} with 2 scans per spectrum, giving a data point every 1.03 seconds using the Nicolet OMNIC series record function. Data was recorded in interferogram format for more rapid recording. GC/IR

data collection type was used with no zero fill, and Happ-Genzel apodization. The spectral range recorded was 4000-450 cm^{-1} .

A special spectrum, the background spectrum (Fig. 3.10), eliminates signals due to the spectrometer and its environment from the sample. It is a single-beam spectrum obtained without a sample in place and with inert gas or solvent in the cell. The background spectrum is the result of the output of the source; the response of the beamsplitter, optics, and detector; and any atmospheric gases inside the optical bench. Each sample single-beam spectrum is ratioed against the background single-beam spectrum so that the absorptions in the final spectrum are due solely to the sample.

The background spectrum accounts for any CO_2 or water vapor within the IR path inside the bench and for solvent/inert in the cell contained in a sample mixture. The background is automatically subtracted from the sample spectrum when it is taken to remove any artifacts. A background was taken using purge air at 600 mm Hg and 82.2°C prior to each series of tests run on a given day. This same background was used for all tests in the series, usually 4-5 in a series. Only FTIR spectra were recorded with the computer. Other parameters, such as boiler temperature, average primary and secondary air flow, and average coal feed rate were obtained manually from the power plant Bailey control system following the completion of all test runs. Because of the inability to directly interface with the power plant control system, this data could not be recorded on a real time basis with the FTIR computer. The air flow was measured from a heated foil across the inlet duct to the primary air fan. Coal feed rate was recorded by a mass feed rate instrument.

Tests were run with the boiler master control, oxygen trim, and limestone feed controls in manual. In manual, the air flow, coal feed, and limestone feed rate control signals were fixed and the feeders or fans did not receive any signals to respond to changes in boiler conditions which might have been caused by the dump of batches of coal or limestone in the tests.

After the boiler controls were set, appropriate data was input into the computer and recording was started. Approximately three minutes of steady state background data were

recorded before the coal was dumped. Twenty four to twenty eight pounds of coal, depending on particle size, were put into the hopper and then dumped by rapidly opening and closing the hopper valve. Data was recorded for 8 to 15 minutes, depending on the particle size of the batch.

When recording was completed, the data was reprocessed from interferogram to absorbance format and saved as Nicolet series (*.SRS) format. A Visual Basic program using Nicolet MACROS/PRO utility calculated gas concentrations from the series data set. The concentration calculations involved sequentially selecting each individual spectrum, subtracting out any water vapor present, performing automatic baseline correct, and using the Quantir quantification methods to quantify the spectra for each of the 6 gases. The concentration and time data were saved in text format. This data was analyzed off-line with Excel, Matlab, or Mathcad, depending on the application.

The heart of the FTIR is the Michelson interferometer, originally designed in 1891 by Albert Abraham Michelson [10, 57, 58, 59] as part of an unsuccessful search for interplanetary "ether". The interferometer (Fig. 3.11) is a device used to generate and control an interference pattern [59]. It consists of a source of radiation energy (s), a beamsplitter (b) to divide the light beam into two parts, a fixed mirror (M1) to reflect one of the two beams back to the beamsplitter, a moving mirror (M2) perpendicular to the fixed mirror to reflect the other beam back to the beamsplitter, and a sample chamber (sc) to hold the sample being investigated [52, 53, 59, 60]. To produce the output interference pattern a light, or radiation, source (s), a detector (d) (which was the eye in early experiments), and a mechanism to displace the moving mirror are needed. The Michelson interferometer divides a radiation beam into two paths and then recombines the two beams after a path difference has been introduced by changing the position of the moving mirror. A movement of the moving mirror by $1/4$ wavelength changes the optical path difference by $1/2$ wavelength. The beamsplitter reflects part of the incident radiation to the fixed mirror, and transmits part of the radiation to the movable mirror. After the beam is reflected off the two mirrors, it is again partially reflected and partially passed by the beamsplitter [58]. The portion of

the beam passed or reflected back to the source is ignored, as it is the combined beam that is of interest.

The presence of a gas which absorbs infrared radiation in the sample chamber will cause some of the radiation passing through the chamber to be absorbed. The amount of radiation absorbed, and the frequencies at which it is absorbed, depends on the molecular structure of the gas and its concentration.

The curve of the output intensity from an interferometer versus the optical path difference (OPD) of the two beams is called the interferogram [59]. Figure 3.12 is an example of a typical interferogram. Initially, consider a monochromatic light source with the fixed and moving mirrors of the interferometer the same distance from the beamsplitter. The beam will be divided in two at the beamsplitter, travel down both arms to the mirrors, be reflected off the mirrors, and recombine at the beamsplitter exactly in phase. As a result, the recombined beam will be at maximum intensity [59]. If the moving mirror is moved by $1/4$ wavelength, the forward and reflected path will be an extra $1/2$ wavelength long, and the recombined beams will be 180° out of phase and at minimum intensity. As the moving mirror is displaced, this pattern of maximum and minimum intensities, and all intermediate intensities, will be repeated.

If the source has multiple wavelengths, each will be modulated in this manner, and the output of the interferometer will be a superposition of these wavelengths. Only when the mirrors are equidistant from the beamsplitter, the zero path difference (ZPD), will all the wavelengths combine to be a maximum. Away from the ZPD the various components of the wavelengths fall out of step and the intensity settles down to an average value. The exact shape of the interferogram is closely connected with the wavelength distribution of the source.

Since the interferogram is recorded on a computer in a digitized form the samples must be taken at equal spacing of path difference and the absolute value of the spacing must be known. This is accomplished on modern FTIR's with a helium-neon laser and a second reference interferometer [58, 59]. The moving mirror of the reference mirror is connected to the moving mirror of the interferometer and the interferogram is sampled at the zero-crossings of the

reference helium-neon laser interferometer. These zero-crossings occur at exact spacing, which establish the path difference for the interferometer.

Fourier transform spectroscopy (FTS) is the technique used to determine a spectrum from the interferometer output power (radiation intensity). Taking the Fourier transform of the interferogram produces a spectrum, which relates interferometer output power to the frequency, which is converted to wavenumber [10, 59]. The interferogram and infrared spectrum of the sample contain the same information, just rearranged. The power of the combined beams in the interferometer is recorded as a function of the phase delay and shows functions that are basically periodic.

System Components

The various components of an FTIR instrument are housed in a unit called the optical bench, or bench for short. An interface card in the computer controls communication between the computer and the bench.

The best broad-band infrared radiation sources for FTIR spectroscopy approximate "black-body" or ideal thermal radiators [59]. The two types of source materials used are ceramics heated to glowing temperature and nichrome wire heated to incandescence. The ceramic units are Globars (a heated bar of sintered silicon carbide) or Nernst glowers (usually an electrically heated hollow tube of zirconium and yttrium oxides).

The detector converts the optical intensity exiting the interferometer into an electrical signal [59]. Detectors are designed to reduce distortion and electrical noise. There are two basic types of detectors in use: thermal and quantum [58, 59].

The sampling of gases is done in gas cells. The simplest cells are glass or metal cylinders with halide windows for the infrared beam to pass through and fittings for the entrance and exit of the gas. The infrared beam passing from the beamsplitter to the detector is directed through the cell to interact with the gaseous sample in the cell. Gas cells are classified as short path or long path, the path length being the length of the infrared beam in the cell which passes through the gas

[57]. Path lengths vary from 5 cm to tens of meters. Short path length cells are used for high concentration gases flowing through a process pipe [57], while lower concentration gases require a long path length cell [57].

The most common type of long path cell is a White cell (Fig. 3.13) [57]. A White cell uses a set of three mirrors to reflect the infrared beam back and forth through a fixed volume of gas. Because the White cell steps the beam back and forth between the mirrors, it has a high path length to volume ratio. One of the limitations of the White cell can be slow response to changes in gas composition, in part due to the lack of uniform overlap between the gas volume and optical path, and in part due to turbulent mixing in the large diameter cell [57]. The larger the cell, the greater this problem.

FTIR Calibration

Quantitative analysis of a specific component in a mixture is accomplished by comparison of the intensity of a unique absorption band with the same infrared band from the pure component of known concentration.

For absorption spectrometry, the law relating spectral band intensity to concentration is the Bouguer-Beer-Lambert law, more commonly known simply as Beer's law [58, 59]. The IR spectrum of a multicomponent mixture is the additive summation of absorption frequencies for all the species present. The presence of a unique, reasonably strong absorption band for each component that is not interfered with by other components is required to establish quantitative analysis.

For a single solute in a nonabsorbing solvent, Beer's law can be expressed as [58]:

$$A=abc \qquad (3.11)$$

where A is the absorbance, a is the absorptivity, b is the pathlength, and c is the concentration. For a multiple component mixture, a series of such equations is obtained for each substance. The K -matrix method (Eqn. (3.12)), also called classical least squares (CLS), is mathematically

$$A=KC \quad (3.12)$$

straightforward, but can lead to indeterminate results for concentration in some circumstances, and the standard spectra recorded to determine the absorptivity must be entirely free of impurities, or the impurities concentrations must be known and used in the calculation [59]. A is the matrix of absorbances at several frequencies of the spectra of the samples used for calibration, K is the absorptivity matrix, and C is the concentration matrix. When the concentration matrix C is known, the absorbance matrix A is found by experiment, and K is calculated. The K matrix is the least squares fit between the observed and calculated absorbances and is often called the calibration matrix.

$$K=AC'(CC')^{-1} \quad (3.13)$$

In the quantification process the absorbance A of the unknown sample is measured at the same frequencies as the calibration was established, and the concentrations of the components are calculated from Eqn. (3.14)

$$C=(K'K)^{-1}K'A \quad (3.14)$$

The concentration is done in this manner, rather than directly inverting C and K because these matrices will be square if no overdetermination is done.

Quantification methods were developed using the CLS (K -matrix) method for CO_2 , CO , SO_2 , NO , NO_2 , and N_2O . Determination of gas concentrations is performed on absorbance

spectra. Calibration standards are gas mixture spectra of known concentration. The standards were prepared from Air Products, Inc. blended mix certified gas cylinders. The accuracy of the certified standards is $\pm 5\%$ of component for 1-99 ppm concentration, $\pm 2\%$ of component for 100 ppm - 0.99% concentration and $\pm 1\%$ of component for 1-49% concentration.

The standards were prepared by mixing various known amounts of different gases in the cell and calculating the concentration of each gas using partial pressures. An MKS model 121 pressure transducer with model 250 controller was used to measure pressure. From 5-12 standards of each gas were prepared, spanning the range of concentrations of that gas found in the flue gas. From the set of standards, Quantir calculated the absorptivity **K** matrix using a regression analysis routine. A separate quantification method was prepared for each gas using a region to single or two-point baseline method. The spectral ranges used for calibration are given in Table 3.2.

Validation of the quantification method is accomplished by Quantir by calculating the percent difference between the concentration predicted from the regression line and the actual known concentration of the sample. All methods had percentage errors less than 5%, except for NO, which had two standards between 14% and 15% errors. Figure 3.14 is a sample plot of the predicted versus actual values for CO.

Figure 3.15 is a reference spectrum of the six gases which were quantified with water vapor removed, spectral range shortened to 2250 - 450 cm^{-1} , and y-axis scale decreased to 1.0 absorbance units, to better reveal the features of slightly absorbing species. This is the portion of the spectrum where all quantification regions are located. In Fig. 3.15, the overlap between SO_2 and N_2O , and CO and CO_2 is clearly seen. The spectral ranges used for calibration were chosen to avoid overlap between gases, avoid interfering water vapor peaks, to keep the absorbance level below 1.5 absorbance units for CO_2 , and to include sharp spectral features, which are better for quantification than smooth slopes. For highly absorbing species, especially CO_2 , shoulders of the spectral features were chosen rather than the large main feature.

Analysis methods

Figure 3.16 is a typical CO₂ profile following batch dump of 26 lb of 16x18 mesh coal into the CFB boiler. A devolatilization peak and rapid exponential decay similar to that seen in bubbling bed tests is seen. However, char burning does not begin until a short time after the completion of devolatilization, as evidenced by the devolatilization decay going to the background level for a few seconds before rising again for char burning. Because char burning in the CFB did not begin until after the completion of devolatilization, the calculation of characteristic times for devolatilization and char burning had to be modified from that used for the bubbling bed data. In Eqn. (2.12), [CO₂]_f is zero (no contribution from char burning during devolatilization), and a plot of ln([CO₂]_R/[CO₂]_i) vs. time yields a straight line whose slope -1/τ_v.

With char burning not starting until the completion of devolatilization, Eqn. (3.5) is modified to delete the contribution of devolatilization CO₂ to the total CO₂ emissions, as shown in Eqn. (3.15), and the calculation of m(t) was not begun until the CO₂ concentration started to rise at the start of char burnout.

$$\frac{m(t)}{m_i} = 1 - \frac{QM_c}{m_i} \int_{t=0}^t \{ [CO_2]_R - [CO_2]_{avg} \} dt \quad (3.15)$$

Plotting ln(m(t)/m_i)^{1/3} vs. time yielded a plot whose negative reciprocal slope was τ_c.

Integrating the transient CO₂ profile and converting the CO₂ concentration to mass of carbon combusted yields a cumulative carbon consumption curve. This curve, Fig. 3.17, plots amount of carbon (whether from volatiles or char) reacted, m_c, versus time,

$$m_c = m_i - m(t) \quad (3.16)$$

where m_i is the total amount of carbon in the sample, and m(t) is the amount of carbon remaining at time t, calculated from Eqn. (3.15).

Figure 3.17 shows three distinct fairly linear regions. The first with the very steep slope is the devolatilization region. The second, immediately following the devolatilization, is the initial char burning region at time t less than τ_c where the CO_2 decay is considered exponential per Eqn. (2.28). The last region is the latter part of char burning where the non-linearities become prominent.

The dashed straight line superimposed upon the initial char burning region is the region over which dm_c/dt was calculated. This value for the entire batch was divided by the number of particles (Eqn. (3.17)) to obtain a per particle burning rate.

$$N = 6m_i / \pi \rho_c d_i^3 \quad (3.17)$$

where m_i is the char mass contained in the batch of coal dumped and ρ_c is the density of the coal.

An alternate method for calculating the characteristic char burning time τ_c can be from the linearization assumption of Eqn. (2.22) combined with Eqn. (2.27) to give:

$$\tau_c = -3m_i / (dm_c/dt) \quad (3.18)$$

3.5 Coals and sorbents evaluated

The types of coal tested were determined primarily by availability. Indiana bituminous and Kentucky coal were used for the laboratory tests, while Illinois washed coal, lignite, and Nova Scotia coal were tested in the power plant. Table 3.3 lists the proximate and ultimate analyses of these coals. The lignite was provided by Ahlstrom Pyropower. Only 100 kg (220 pounds) was provided, so the number of tests which could be conducted was limited.

The following double screened Tyler standard mesh sizes were tested in the laboratory: 3.5x4, 4x5, 5x6, 6x7, 7x8, 8x10, 10x12, 14x16, 16x18, and 18x20. Particle sizes were taken to be the average screen opening between two consecutive sieve sizes.

The particle sizes tested in the CFB boiler at the power plant were chosen to span the range of coal sizes typically burned. The coal is crushed to 0.952 cm (3/8 in.) top size, so that was chosen as the upper limit. The lower limit was chosen as 20 mesh, as this was near the smallest size particles (1.0 mm) tested by Christofides and Brown [11]. Double screened mesh sizes were 3/8"x4, 4x6, 6x8, 8x10, 10x14, 14x16, 16x18, and 18x20.

Sorbent testing was done on three limestones. A large majority of the testing was done using limestone from the Gilmore City formation which was obtained at the ISU power plant. This limestone is a coarse, porous limestone of an intermediate geological age, i.e. the Mississippian age. A chemical analysis of the three limestones is given in Table 3.4. Chemical analyses were done on two sizes of Gilmore City formation limestone to check for any differences attributable to the crushing process. Limestone was sized using Tyler U.S.A. series sieves into sizes ranging from 0.125 to 4.75 mm. A size distribution analysis for the Gilmore City limestone as delivered to the power plant is shown in Fig. 3.18. The Gilmore City limestone was also separated into three color groups to compare the variation in sorbent performance in one type of limestone.

In general, limestone was used for the sorbent tests, but for several testing applications calcined limestone (lime) was used. When this was done limestone particles of substantially larger size than the sand were batched into the bed at the prescribed operating temperature but with no SO_2 injected. After calcination was complete the bed was quickly cooled and the removed from the combustor. The particles were removed from the bed using a sieve of a size between the size of the limestone and the sand. Some of these calcined particles were analyzed for surface area and pore size distribution of the calcine. After weighing the recovered mass, the limestone particles were subsequently used in sulfation tests.

4. EXPERIMENTAL RESULTS

4.1 Laboratory reactor tests

Devolatilization

A typical CO_2 profile for a batch test of 5g 7x8 mesh Kentucky coal in the laboratory scale bubbling fluidized bed combustor is shown in Fig. 3.2. The trace peaks sharply, as devolatilization and char burning begin, drops rapidly as volatiles are exhausted, and then gradually declines as char is slowly consumed. According to Eqn. (2.12), the characteristic devolatilization time, τ_v , can be determined from the slope of the CO_2 trace immediately after the peak concentration. The parameters $[\text{CO}_2]_f$ and $[\text{CO}_2]_i$ are determined by drawing asymptotic lines along the "devolatilization" and "char-burning" sections of the CO_2 trace, respectively, as illustrated in Fig. 3.2.

Total devolatilization times, $t_v = 3\tau_v$, for Indiana coal as a function of initial particle diameter, d_i , in the range of 1.0 to 6.2 mm are plotted in Fig. 4.2 along with devolatilization times from Essenhigh's [6] relationship. The devolatilization time for particles larger than 4 mm closely approach Essenhigh's relationship, but are 6-40% larger than those predicted by Ragland and Weiss' formula [8]. Since coal rank does not affect the dependence of devolatilization time on the initial particle size [5, 8], the differences between the time constants in this study for particles larger than 3 mm and the Ragland and Weiss [8] relationship are attributed to differences in coal particle shapes. The latter researchers [8] used approximately spherical coal particles in their experiments. The experiments in this study, much like Essenhigh's [6], used coal particles that were produced by crushing and screening the parent coal and resembled cubes or wedges. Differences in particle sphericity, i.e. particle shape, may affect the mass transfer of volatile matter from the particle, thus altering the power law dependencies of devolatilization time on initial particle size.

The discrepancies at smaller diameters (less than 4 mm) are artifacts of the gas sampling system and are expected to arise whenever characteristic times for devolatilization are comparable to or smaller than the lag time of the gas sampling system. The fluidized bed combustor and the gas analysis system can be treated as two CSTRs in series (dead time due to plug flow in the sampling lines does not affect the analysis). The net response of the system at the gas analyzer during the coal devolatilization is described by:

$$\frac{[CO_2]_A - [CO_2]_f}{[CO_2]_i - [CO_2]_f} = \frac{\exp\left(-\frac{t}{\tau_v}\right) - \exp\left(-\frac{t}{\tau_I}\right)}{1 - \frac{\tau_I}{\tau_v}} \quad (4.1)$$

Step tests on the gas analysis system using CO₂ as a tracer gas showed that it behaved as a first-order system with characteristic lag time, τ_I , equal to 3.0 s.

Assuming τ_v is greater than τ_I , a semi-logarithmic plot of non-dimensionalized CO₂ concentration versus time will give a straight line with slope equal to the negative reciprocal of τ_v for times long compared to τ_I . This appears to be the case in Fig. 4.2 for particles larger than 4 mm diameter. However, for smaller particles where τ_I is greater than τ_v , the system response will have a time constant closer to τ_I than τ_v . This behavior is evident in Fig. 4.2, which shows the measured devolatilization times converging to approximately $3\tau_I$ for the smaller particles. Measurement of devolatilization times t_v less than 9 s (i.e. for particles less than 4 mm) will require a CO₂ gas analyzer system with a significantly faster response than the present system.

Char burning

To validate the methodology, the characteristic times for char burning, τ_c , were measured as a function of initial particle diameter of batched coal samples. The data was interpreted by preparing a plot of $\log(\tau_c - \tau_I)$ vs. $\log d_i$ as shown in Fig. 4.3. The constant τ_I was determined from Eqns. (2.20) and (2.21) by plotting τ_c vs. mass of char in the coal batch, m_i , for a fixed

particle diameter [9]. As a second check of the methodology, the burnout times, t_c , were estimated as the time the transient CO_2 signal disappeared into the steady-state background CO_2 signal. Although the magnitudes of τ_c and t_c from a particular test should be different, the dependence on initial diameter was expected to be the same.

For the relatively large particles tested, the slope of Fig. 4.3 was expected to be 2 (the "d-squared" law of mass-transfer limited kinetics) or at least 1.5, which is typical of mass-transfer limited kinetics with variable Sherwood number. Instead, a slope of 1.32 was found. The slope from the t_c data is 1.31, except for the largest particles which displayed a much smaller slope. This large particle behavior was attributed to the inability to estimate burnout times from the weak, residual signal generated from large, slow-burning particles as burnout was approached. The agreement between τ_c and t_c data for smaller particles suggests that the methodology was sound but that the coal was behaving in an unexpected manner.

The first hypothesis was that chemical kinetics was playing a stronger role than anticipated. Previous researchers [6, 8] who have observed power laws ranging from between 1 and 2 attribute this behavior to the combined effects of chemical kinetics and mass transfer. To test this hypothesis an attempt was first made to measure activation energies of char burning by varying the temperature at which the coal batch tests were performed (Table 4.1). A semi-logarithmic plot of reciprocal $\tau_c - t_i$ vs. reciprocal bed temperature, shown in Fig. 4.4, yielded an apparent activation energy of approximately -5.5 ± 2.6 kcal/mol. Also shown in Fig. 4.4 is a semi-logarithmic plot of reciprocal $t_c - t_i$ vs. reciprocal bed temperature which yields an activation energy of -0.076 ± 0.5 kcal/mol. If chemical kinetics are rate limiting, a positive activation energy closer to 40 kcal/mol is expected. These results indicate a very small activation energy at best, which suggests that mass transfer to the particle controls char burning in these experiments.

Further evidence that chemical kinetics is not rate-limiting is found in the ratio of $(t_c - t_i)/(\tau_c - t_i)$ reported in Table 4.2 for Indiana coal. A ratio approaching unity is expected for chemical kinetic control (Table 2.1) whereas most tests show ratios between the 0.50 and 0.66 range expected for mass transfer limited reaction.

The second hypothesis was that primary fragmentation [6, 8, 9, 15] is responsible for the smaller than expected exponent. This hypothesis was developed from an analysis on the burnout time of fragmented particles. Although an oversimplification of the actual process, it was assumed that fragmentation produces N_f spherical fragments, all of diameter d_f . Accordingly, the diameter of the fragmented particles is related to the initial particle diameter by:

$$\frac{d_f}{d_i} = \left(\frac{1}{N_f} \right)^{\frac{1}{3}} \quad (4.2)$$

This formulation, despite its simplifying assumptions, is nevertheless consistent with experimental results of Chirone et al. [15]. Furthermore, the number of fragments is expected to increase with particle size [6, 15]; Chirone et al. [15] report a near linear dependence for a South African bituminous coal. Assuming a linear dependence of N_f on d_i (i.e. $N_f \propto d_i$) in Eqn. (4.2) the following is obtained:

$$d_f \propto d_i^{2/3} \quad (4.3)$$

Mass transfer limited combustion with constant Sherwood number predicts that the characteristic time for combustion increases with the square of fragmented particle diameter. Consequently, the apparent power law due to burning of coal fragments will be:

$$\tau_c \propto d_i^{4/3} \cong d_i^{1.33} \quad (4.4)$$

Hence, the power law obtained is consistent with the occurrence of particle fragmentation.

The test for this hypothesis was to recover char fragments soon after batching coal samples to the fluidized bed and compare the size distribution with the original distribution of the charge. During this test, 40 g of 2.18 mm Indiana coal were batched into the bed which was

heated with propane at around 1116 K and 1 m/s. After devolatilization was over (~20-25 s), air and propane were shut off and a small flow of nitrogen gas was introduced to quench the combustion. The bed was slowly cooled to room temperature using more nitrogen gas. The char that remained in the bed was then recovered and sieved to obtain the size distribution of char fragments. As Fig. 4.5 illustrates, the 2.18 mm-dia. coal produces a large number of fragments during volatiles release. The average size of these fragments was estimated to be 1.81 mm, which is around 84% of the original diameter of coal particles. A second quench test with 50 g of 4.38 mm coal produced fragments that had average size close to 3.07 mm (around 70% of the original size) and a much wider size distribution (see Fig. 4.5). These tests verify that significant fragmentation occurs and that the extent of fragmentation increases with particle diameter. These observations are in accordance with the experimental data of Chirone et al. [15].

Population balance results for char burning

Coal samples were loosely classified as "small" (~ 1 mm) or "large" particle (~ 5 mm) for these experiments. The distinction pertains to the degree of fragmentation the particle experiences when it first enters the combustor. Chirone et al. [15] survey recent fragmentation research, including work describing size dependent characteristics in bituminous coals. For Indiana bituminous coal, small particles do not fragment whereas large particles readily fragment. As might be expected, primary fragmentation has a profound effect on the impulse response. For this reason, the results are divided along small particle and large particle distributions.

In this study, small particle distributions are defined as those with particles small enough where fragmentation is negligible but are not so small that chemical kinetics become rate-limiting (as with pulverized coal). A typical impulse response for a small particle block distribution is presented in Fig. 4.6. Initially, the CO₂ transient is dominated by combustion of volatiles. However, this transient response decays roughly as fast as the instrumentation response, making separation of signals difficult. The remainder of the transient response characterizes char

combustion. Unlike the volatile response, char combustion is slow enough that the instrumentation can adequately track the signal.

An unusual feature of the char transient is the change in curvature from a negative second derivative to a positive second derivative. These characteristics are also present in Eqn. (2.55) and (2.56). The former has a negative-definite second derivative, while the latter has a positive-definite second derivative, with the curvature change occurring at $\tau = d_{\min}^2/2f$, the time at which the smallest particles burn out. Physically, because smaller particles approach zero faster than larger particles, a block distribution initially expands, creating a negative second derivative. This distribution expands until the smallest particles burn out. After that, the distribution can only contract, resulting in a change of curvature.

Although $K(t)$ is uniformly continuous for $0 \leq t \leq d_{\max}^2/2f$, the first and second derivatives are piece wise continuous in this interval. A jump discontinuity occurs at $t = d_{\min}^2/2f$; therefore, in a strict sense, $K(d_{\min}^2/2f)$ is not a point of inflection. This discontinuity occurs because a block distribution has well-defined edges. In practice, these edges are fuzzy, which smooths discontinuities and produces a response with a point of inflection. Therefore, with a slight abuse of terminology, $K(d_{\min}^2/2f)$ will be referred to as a point of inflection.

A point of inflection at $t_i = d_{\min}^2/2f$ suggests that t_i decreases as $d_{\min}$ decreases. To test this hypothesis, several block distributions were formed where $d_{\max}$ was held constant and $d_{\min}$ was varied. So that a uniform distribution could be better approximated, consecutive screen samples were combines, each with a mass fraction:

$$x_i = \frac{\phi_o \Delta d_i}{\sum_{i=1}^N \phi_o \Delta d_i} = \frac{\Delta d_i}{\sum_{i=1}^N \Delta d_i} \quad (4.5)$$

where Δd_i is the difference between the top and bottom particle sizes in each sieve. Small particle tests were carried out for 16x18 through 16x30 mesh coal; mass fractions for (nearly) uniform particle distributions are presented in Table 4.3. Since all tests were run with 5-g samples, ϕ_o

decreases as the distribution widens. In Table 4.3, different initial block distributions are denoted by a superscript index. For example, mass fractions for 16x20 mesh coal are listed in the column labeled ϕ_0^2 .

Equations (2.55) - (2.57) were fit to experimental data sets. Given $d_{\max}$, coefficients $d_{\min}$, ϕ_0 , and f were estimated by minimizing the sum square error with a fourth-order, downhill simplex [62]. So that the simplex would converge to realistic values, and exponential penalty function enforced the following constraints:

$$0 < d_{\min} < d_{\max} \quad (4.6)$$

$$f > 0 \quad (4.7)$$

$$\phi_0 > 0 \quad (4.8)$$

Results are presented in Table 4.4, and selected data sets are plotted in Figs. 4.7 and 4.8. Some discrepancies exist between the sieve data and the simplex estimates. Most of the error can be ascribed to insufficient knowledge of the actual particle distribution. When coal is sieved, many different shapes of coal, including shards and slivers, are classified as spheres with diameters bounded by the mesh openings. However, despite these discrepancies, experimental data follow theoretical trends well.

When large particle bituminous coal enters a fluidized bed, some particles shatter, a process referred to as primary fragmentation. Primary fragmentation - caused by thermal shock and devolatilization - occurs quickly [16], and the resulting fragmented distribution guides the impulse response. As such, the effective initial mass distribution is the fragmented distribution [63]. However, because the fragmented particle distribution is not known beforehand, impulse responses for large particles are difficult to predict.

To examine the effects of fragmentation on the impulse response, two consecutive tests were performed: one to acquire the impulse response and another to obtain an estimate of the

fragmented particle distribution. Fragmentation data from the second test was then used to model the impulse response of the first test.

A 40 g sample of 3.5x4 mesh (4.75-5.60 mm) coal was divided into two, 20 g samples. One sample was batched into the combustor, and the transient response was recorded. When this transient response had decayed to zero, the second sample was batched into the combustor. After the volatile response had subsided, the bed was quenched with nitrogen. When the bed had cooled, char particles were separated from the bed material and screened. The cumulative char distribution, along with a continuous estimate, is shown in Fig. 4.9; the derivative of the cumulative distribution, $\lambda(d, 0^+)$, is shown in Fig. 4.10. A noteworthy feature of $\lambda(d, 0^+)$ is the jump discontinuity at $d \approx 4.00$ mm. This discontinuity is a separation between particle fragments ($d < 4.00$ mm) and unfragmented particles ($d > 4.00$ mm).

Because the coal samples came from the same stock, the particle distribution for the impulse response was assumed to be proportional to the distribution obtained from the quench test. That is, for some constant, k ,

$$\phi(d_o) = k\lambda(d_o, 0^+) \quad \forall d_o \quad (4.9)$$

Given $d_{\max}$ and $\lambda(d, 0^+)$, coefficients f and k were adjusted to fit the experimental data. Results for $f = 2.1 \times 10^{-2} \text{ mm}^2/\text{s}$, and $k = 0.96$ are illustrated in Fig. 4.11.

For large char particle distributions, the combustion rate coefficient is significantly greater than those estimated for small particle distributions. The differences in rates likely reflect the differences in (effective) Sherwood numbers. For $f \propto \text{Sh} \propto \text{Re}^{1/2}$, increases in the particle diameter accompany increases in the mass transfer rate. This explanation is complicated somewhat by the wide distribution of fragmented coal particles. However, if the mean diameter of the small particle distributions is taken as 1 mm and the mean diameter of the large particle distribution is taken as 4.5 mm, the expected ratio of combustion rate coefficients is 2.1. This ratio is close to the experimental ratios, which range from 2.0 to 2.3.

Besides the combustion rate coefficient, the other item worth examining is the curvature of the char response. Some curvature differences exist between the experimental data and the theoretical impulse response. These deviations can be corrected by slightly adjusting the curvature of $\lambda(d,0^+)$. Adjusting the curvature of $\lambda(d,0^+)$ is warranted in that the differences in the impulse responses are likely due to slight differences in the fragmented particle distributions between the test runs. However, curvature deviations notwithstanding, the population balance equation provides useful insights into the combustion dynamics of large char particles.

Calcination

In this study, experiments were done to examine the change in calcination time constants and in the extent of calcination under various conditions. The effects of particle size, CO_2 concentration, temperature and flow velocity were all examined. Additionally, testing was conducted in the lab using two additional types of limestone provided by Ahlstrom Pyropower. Analysis was made by comparing simplified results for controlling mechanisms as discussed in section 3.2.

Comparison of transients to the calcination model

The full model developed to describe calcination is a shrinking particle core model, as described by Eqns. (2.62) through (2.65). These four differential equations were solved numerically using the program code listed in the appendix. This calcination model was also simplified in section two into Eqns. (2.67) and (2.68).

Figure 4.12 shows how the full model was fit to the transient data for two different particle sizes. Curve fitting was not successful using a single value for k_c and D_{ec} for a range of particle sizes. The curve fits shown in Fig. 4.12 were made by varying D_{ec} between the particle sizes. For model runs using a bed temperature of 1123K, a fit to the slope of the experimental transient was made for all particles sizes using a k_c value of 0.1 m/s. The model predicts values of D_{ec} ranging from $1.67 \times 10^{-4} \text{ m}^2/\text{s}$ for 0.55 mm particles to $3 \times 10^{-5} \text{ m}^2/\text{s}$ for 2.58 mm particles. This

result either indicates that the model predictions do not satisfactorily describe calcination, or that the effective diffusivity varies between particle sizes. Particle analysis suggests that sintering early in the reaction may actually cause this decrease in diffusivity for the larger particle sizes. As the particle radius increases, the time to complete calcination increases. This allows more time for sintering to occur. Examination of four particle sizes using the model requires D_{ec} to be increasingly smaller as the particle size increases.

The values obtained by curve fitting do not correspond well to those found in the literature. Borgwardt [64] and Dennis and Hayhurst [22] found values of k_s around 0.01 m/s. Milne *et al.* [28] found that the shrinking core mechanism did not accurately describe calcination. Values for D_{ec} were high when compared to theoretical calculated values. The value of D_{ec} equal to $1.67 \times 10^{-4} \text{ m}^2/\text{s}$ as shown in Fig. 4.12 for the 0.55 mm particle size is the value found for bulk diffusivity of CO_2 in nitrogen. This is much higher than expected. It must be presumed that diffusivity in the freshly calcined layer is not controlled by Knudsen diffusivity, which would result in a much lower value of D_{ec} .

The numerical solution allows for the evaluation of the controlling resistances during the transient. Figure 4.13 shows the solution for the batch addition of 0.55 mm limestone shown in Fig. 4.12. The chemistry resistance is much higher than any of the other resistances. At a temperature of 1123 K this particle size is controlled by the chemical reaction rate. There is some bed mixing resistance early in the reaction, but it is not significant. In contrast to this, Fig. 4.14 shows the resistance plot model run shown in Fig. 4.12 for the 2.58 mm particle size. Since diffusivity is much lower, the pore diffusion resistance is equal in significance in the latter part of the transient. Thus, for larger particles, the lower predicted diffusivity leads to a situation where both chemical reaction and diffusion are involved in limiting the reaction rate.

Effect of particle size on calcination

The effect of particle size on the calcination time constants and the extent of calcination was investigated. In chapter three, the full calcination model was reduced to simplified

expressions for the calcination time constant. These expressions help to indicate the controlling mechanism for calcination. In this investigation, chemical-reaction and pore-diffusion control were considered directly using equations from section 3.2.

Data from tests with four particle sizes at seven temperatures were changed into the form of Equation (2.76) for analysis of τ_c . Results from four of these tests are shown in Fig. 4.15. In this figure τ_c can be determined from the reciprocal of the slope. The data should plot as a straight line for early times if calcination is chemistry-controlled. The lines for the data in Fig. 4.15 are fairly straight over the length of the data. A slight upward curvature is apparent in these data and in most of the results.

If chemical reaction controls calcination, τ_c should vary directly with particle diameter. Results for tests conducted with 30 gram batches of four particle sizes are shown in Fig. 4.16. These tests were conducted at seven different temperatures. In these tests the value of τ_c was determined using Eqn. (2.76) for chemical reaction controlled calcination. Figure 4.16 shows that τ_c is proportional to particle size at lower temperatures, but has an increasing power law dependence as temperature is increased. The regressions shown in Fig. 4.16 show a particle size dependence of from $d_p^{.91}$ to $d_p^{1.62}$, with the particle size dependence increasing with temperature. The values of the particle size dependence for each temperature are shown in Table 4.5.

The deviation from d_p^1 dependence in the tests could be caused by one of two factors. Both film diffusion and pore diffusion could possibly result in higher particle diameter power laws. Analysis for the time constant associated with the rate of change of the dimensionless core radius for film diffusion control, as developed in Eqn. (2.80), is $\tau_{ch} = d_p/c_{lc}h_c$. However, h_c also has a particle size dependence between $1/d_p^{1/2}$ to $1/d_p$. This is evident by analysis of the two correlations used in the model. The first was a correlation for the Sherwood number, Sh , developed by Froessling for isolated spheres [65]:

$$Sh = \frac{h_c d_p}{D_{ec}} = 2 + 0.6 Re^{\frac{1}{2}} Sc^{\frac{1}{3}}, \quad (4.10)$$

where Re is the Reynolds number, ud_p/ν , and Sc is the Schmidt number, D_{AB}/ν . The other correlation used was developed by La Nauze for char combustion in fluidized beds [66]:

$$Sh = \frac{h_c d_p}{D_{ec}} = 2\varepsilon_b + 0.69 Re^{\frac{1}{2}} Sc^{\frac{1}{3}}, \quad (4.11)$$

where ε_b is the bubble voidage in the bed. This makes the overall size dependence of the film diffusion time constant $d_p^{1.5}$ to d_p^2 . Since film diffusion cannot be the controlling mechanism based on a non-constant transient, the overall time constant would have a smaller dependence. Additionally, the effect of film mass transfer would diminish over time, since the other resistances are increasing while film diffusion resistance is decreasing in Eqn. (2.69) and constant in Eqn. (2.70).

Pore diffusion could also play a role in the result of time constants which are greater than one. An exact particle size dependence cannot be extracted for the value of τ_c since it is based on chemistry-controlled calcination from Eqn (2.76). It is believed that a particle size dependence greater than one could indicate pore diffusion control because the time for complete conversion for this case equals two. This is shown in Levenspiel [33], and corresponds to a chemistry-controlled time for complete conversion size dependence of one. Use of Eqns. (2.89) and (2.90) which describe pore-diffusion controlled calcination for flat plates was analyzed, but the data in these forms did not form a straight line which could be systematically measured. Numerical solution of the full model indicates that pore diffusion may give a significant resistance to reaction.

Deviation from a d_p^1 relationship for τ_c becomes more apparent at higher temperatures. At these temperatures, chemistry is no longer rate limiting, and transition to the "d-squared" dependence of diffusion becomes apparent. This might indicate that diffusion resistance may become significant at the higher chemical reaction rates associated with these temperatures. It is

also interesting to note how the curves for the three highest temperatures begin to coincide. The chemical reaction rate temperature dependence is governed by an Arrhenius relationship, i.e. k is proportional to $e^{-E/RT}$. This temperature dependence is greater than that for diffusion control, e.g. bulk diffusivity is proportional to $T^{3/2}$. An observed activation energy determined for a diffusion process would be the value for species transport, approximately given by $E_a = 3RT/2$, which is around 3 kcal/mol for these temperatures. The fact that the τ_c vs. particle diameter curves of Fig. 4.12 begin to coincide at higher temperatures may be explained by the lower temperature dependence for diffusion. This strengthens the argument for pore diffusion control at higher temperatures which is evidenced by a higher particle size dependence.

Effect of temperature on calcination

The same data which were considered for particle size effects are plotted in Fig. 4.17 as $1/\tau_c$ vs. $1/T$. Fitting straight lines through this data on a log-linear scale gives activation energies for calcination ranging from 29.5 to 45.5 kcal/mol. The fit is relatively good considering the small number of data points for these regressions, which consist of five to seven points per particle size. Table 4.6 shows the activation energies and the 90% confidence interval associated with the data. Activation energies range 29.5 to 45.4 kcal/mol. The activation energy decreases as the particle size increases. Within the uncertainty supported by 90% confidence intervals, the difference in activation energies between adjacent particle sizes is not significant. However, when the largest particle size (2.58 mm) is compared to the two smallest sizes, there does appear to be a significant difference in activation energies.

This conclusion is confirmed by performing a t-test on the slopes of these activation energy curves. The null hypothesis in this case was: "There is no significant difference between the slopes (activation energies) for different particle sizes." The alternate hypothesis is: "The slope (activation energy) for the larger particle size is less than that for the larger particle size." The statistical analysis for this t-test corresponds to the t-test for two means given in Kennedy and Neville [67], and the t-test to find the significance of the slope found in the same reference. It

involves finding the variance of the residuals for each line, which is determined by:

$$s_{y|x}^2 = \left(\frac{\sum \varepsilon_i^2}{n-2} \right), \quad (4.12)$$

where ε_i^2 represents the square of the residuals. The combined variance of the two slopes being compared, $s_{y|xc}$, is computed from:

$$s_{y|xc}^2 = \frac{s_{y|x1}^2(n_1-2) + s_{y|x2}^2(n_2-2)}{(n_1-2) + (n_2-2)}. \quad (4.13)$$

The standard deviation for the difference of the slopes is then determined by:

$$s_{bd} = s_{y|xc} \sqrt{\frac{1}{s_{x1}^2(n_1-1)} + \frac{1}{s_{x2}^2(n_2-1)}} \quad (4.14)$$

The t-statistic is then found from:

$$t = \frac{|b_1 - b_2|}{s_{bd}} \quad (4.15)$$

This t-statistic is compared to the one tailed t-distribution value for (n_1-2+n_2-2) degrees of freedom to determine the validity of the null hypothesis.

In these t-tests the slope (activation energy) of the 0.55 mm particles was higher than the 1.55 mm particle activation energy at a 6% level of significance. The 0.55 mm slope was higher than the 2.58 mm slope with 1% level of significance. Statistically, the activation energy is decreasing as particle size increases.

This trend of decreasing activation energy with increasing size is not unexpected.

Observed activation energies may differ from the true chemical rate activation energy due to diffusion processes. Pore diffusion in catalyst particles gives observed activation energies which are $1/2$ of the true value for uni-modal pore distributions and $1/4$ of the true value of bimodal distributions. Film diffusion processes will give low activation energies (1-3 kcal/mol) due to temperature effects on bulk or Knudsen diffusivities [68].

Analysis of the effect of temperature for gas-solid reactions as considered by the shrinking core model is significantly different than the results for catalyst pellets. In the shrinking core model the reaction does not occur in the volume of a pellet, but at a receding interface. Thus, the activation energy varies between the chemical activation energy and the low activation energy associated with film diffusion.

The activation energies for the smaller particles approach results in the literature for chemically controlled calcination. Borgwardt [38] estimated activation energies for small particles (1-10 μm) of 48-49 kcal/mol. Powell and Searcy [69] also estimated activation energies for calcination of 49 ± 3 kcal/mol.

Khraisha and Dugwell [20, 70] determined activation energies in a thermogravimetric analyzer (TGA) and in a suspension reactor for 40-90 μm Cauldron limestone particles. In the TGA they obtained activation energies between 98 and 350 kcal/mol depending upon sample mass and heating rate in a simulated combustion atmosphere. When using a suspension reactor they obtained 47 kcal/mol. The conclusion they draw is that TGA analysis may give misleading values for activation energy due to slow mass transfer.

All of the aforementioned investigators, who used smaller particle sizes than were used in the present study, concluded that calcination rates were chemically controlled. In the laboratory FBC experiments, the smaller particles exhibited chemically-controlled calcination; however, the larger particles had reduced activation energies, and may be controlled by processes other than chemical reaction.

Both particle size and temperature appear to have relatively little impact on the extent of calcination. The extent of calcination is determined from Eqn. (3.9). Figure 4.18 shows the

extent of calcination five minutes into the transient for the data which was discussed for particle size dependence and activation energy calculation. The extent of calcination shown is around 80% for a large portion of the data. In Fig. 4.18, calcination reaches its greatest extent at around 1123 K, which is often cited as the optimum temperature for sulfur sorption. A carbonation reaction, the reverse of Eqn. (2.58), is the most conceivable mechanism to limit the extent of calcination to less than 100%, since pore plugging due to sulfation does not occur until later times in the reaction.

Effect of CO₂ concentration on calcination

Five experiments were run to determine the effect of background CO₂ concentration, [CO₂]_i, on the reaction rate. In Table 4.7, the calcination time constant, τ_c , as reported for five different values of [CO₂]_i. These tests were conducted by flowing CO₂ from a cylinder and reducing air flow to maintain a temperature of 1123 K and a superficial velocity of 1.5 m/s. SO₂ was not added in these experiments. The calcination time constant increases slightly with increasing background CO₂ concentration, a result consistent with the work of other researchers [22, 25, 70]. This result is also consistent with the analysis for τ_c found for chemistry-controlled calcination. In Eqn. (2.76) it was determined that τ_c should be inversely proportional to {[CO₂]_E - [CO₂]_i}, which it is.

Effect of superficial velocity on calcination

A series of experiments were done to examine whether superficial velocity in the bed affected τ_c . Table 4.8 shows the results of five experimental runs which were conducted at different flow velocities. In this experiment τ_c was around 32 seconds for most of the runs. The calcination time constant of 42.1 seconds for the run at 1.66 m/s appears to be an outlier. Neglecting this point, a 95% confidence interval on the mean of the remaining four points gives a value for τ_c of 32.0 ± 1.1 seconds. More runs would be required to validate this value. If film diffusion had an important role in calcination, an increase in superficial velocity would cause τ_c to

decrease. Thus, it is unlikely that film diffusion resistance is significant in the calcination process within a fluidized bed. The effect of u_o on the mass transfer coefficient is small at the low values of Re_d used (approximately 6 to 9). In these correlations, that is Eqns. (4.10) and (4.11), velocity is raised to the $1/2$ power in the Reynolds number term.

Calcination results for different limestone types

Transient analysis experiments were also conducted on two other types of limestone beside the Gilmore City Formation limestone from the I.S.U. power plant. Figure 4.19 plots the CO_2 concentration above background vs. time for the Nova Scotia and Cedar Bay #1 limestones. The transients shown are typical of results for other particle sizes in that the Nova Scotia limestone has a lower peak CO_2 concentration, and returns more slowly to background than the other limestones. Table 4.9 shows calcination and sulfation results for 25 tests done with varied particle sizes at $T_{bed} = 1123$ K, $U_o = 1.06$ m/s, and a batch size of 20 grams of limestone. The Nova Scotia limestone generally has a higher extent of calcination and a higher calcination time constant than the Cedar Bay #1 limestone. The reason for this is not clear. It may involve the magnesium content of the stone, and its effect on diffusion characteristics and particle sintering. Calcination data for the Gilmore City formation limestone was invalidated by excessive drift in the CO_2 meter for the 20 gram batch mass used in this comparison.

Scanning Electron Microscope (SEM) analysis of calcined particles

Another phase of this study involved analysis of particles which were extracted in the middle of the calcination process. Reflected and transmitted light microscopy and SEM analysis of particle cross sections reveal an inner core for particles removed during the calcination transient. Some particles also reveal two zones within the outer calcined ring. The calcination process can be illustrated fairly thoroughly by examination of SEM photographs for a single particle extracted in the middle of the reaction.

To fully appreciate the structural changes that take place during calcination, it is important

to see the physical nature of the limestone being calcined. Figure 4.20 is an SEM photograph of a thin section of Gilmore City formation limestone. The SEM photograph does not show the oolitic formation in the same detail as is seen using the transmitted light microscope. Nevertheless, with a close examination circular structure of the oolites can be observed. The limestone is seen to have a featureless compact structure. There appears to be little porosity in the limestone prior to reaction.

Figure 4.21 is an SEM photograph of a particle extracted two minutes after addition of 150 grams of 2.58 mm limestone. The appearance is very different from that of the unreacted limestone. The center region, which has a light color, contains CaCO_3 which is in the process of calcining. The compact structure of the limestone is giving way to a coarse, broken structure. The darker intermediate region and the outer bright region have undergone calcination. The darker region has been calcined more recently and the outer region has undergone some further structural changes.

Further detail of this particle is shown in Figs. 4.22 - 4.25. Within the calcination core there is a region that has retained a compact structure. The section identified as Region A in Fig. 4.21 is shown in greater detail in Fig. 4.22. An interesting feature of this region are the holes that are present in the center of the picture. This appears to be outgassing at the start of the structural transformation that occurs during calcination. Another location within the CaCO_3 core is shown in Fig. 4.23. In this region the limestone structure has become broken and jagged. It is apparent from these pictures that although the shrinking core model assumes a reaction at the surface of an unreacted core, some reaction is taking place within the core.

Structural changes also appear to be taking place within the calcined regions. The section of Fig. 4.21 identified as Region C is shown more fully in Fig. 4.24. In this region the sub-particles have become smaller and apparently smoother. This change in size and structure of the particle makes focusing the SEM more difficult. The structure seems highly porous. Near the center of the picture it appears that some of the small particles are sticking together. The sintering effect is noticeably more complete near the surface of the particle. Fig. 4.25 shows

Region D of Fig. 4.21. In this region the pores have become smaller and the sub-particles seem to be conformed to one another. The bright region to the left of the particle is a result of sulfation beginning to take place at the particle surface.

This analysis suggests that initially during calcination a large surface area is formed. After a period of time the calcine sinters and loses much of its surface area. Several investigators [28-30] have studied the effects of calcination time and temperature on surface area. Higher temperatures in the outer portion of the particle may cause increased sintering rates. The importance of this finding is that increased surface area near the particle surface may cause higher sulfation reaction rates early in the transient. It is assumed that initially calcination takes place on the outer surface of the particle, and it produces the high surface area calcine that is characteristic of the intermediate region of Fig. 4.21. This would affect the size and formation of a sulfation reaction zone.

Surface area analysis of calcined particles

Surface area measurements were made on Gilmore City formation limestone calcined in the laboratory FBC at temperatures of 1200 K and 1123 K. These measurements were made on particles from 150 gram batches of limestone which were calcined in the combustor for 12 minutes. By the time of their extraction, the CO_2 concentration had returned to background for several minutes. Calcination at 1200 K resulted in a specific surface area of $11.32 \text{ m}^2/\text{g}$ using a nitrogen adsorption method, and $14.03 \text{ m}^2/\text{g}$ using a nitrogen desorption method. The surface area of the lime calcined at 1123 K was measured to be $13.86 \text{ m}^2/\text{g}$ and $15.28 \text{ m}^2/\text{g}$ for nitrogen adsorption and desorption methods, respectively. This result suggests that sintering is more significant at higher temperatures.

Pore volume distributions for both samples show that the most of the pore volume generated in calcination surface area is created in pores with diameters of less than $0.1 \mu\text{m}$. At higher temperatures the pores created have a larger diameter than those created at lower temperatures. The average pore diameter from BET analysis for the 1123 K particles was 0.0576

μm , while particles calcined at 1200 K exhibited a mean pore diameter of 0.0760 μm . The sintering process is clearly temperature dependent. Quantitative analysis of the differences in surface area within a single partially-calcined particle is probably not possible. However, Fig. 4.21 seems to indicate that the calcine near the CaCO_3 core has a higher surface area than the calcine near the particle surface. Thus early in the sulfation transient the outer surface has a higher surface area but a smaller mean pore diameter. This may result in increased sulfation reaction rates early in the transient.

Sulfation

An aim of this study was to develop methods to use transient gas analysis to characterize the sulfation process. As a first step toward this goal, a numerical model was developed to analyze the mechanisms of sulfation. This model was used to characterize the sorbent by fitting experimental data to the numerical solutions. The reaction rate coefficient, the effective diffusivity and the pore plugging time constant were determined by fitting this model to data from the laboratory combustor. After the numerical model results were validated, the simplifications discussed in chapter three were made in order to analyze data analytically for controlling mechanisms. Many transient batch tests were conducted with a range of particle sizes, temperature, oxygen concentrations, and types of limestone. The simplified expressions for controlling mechanisms were applied to these data.

Comparison of transients to the sulfation model

The model developed to describe sulfation is a shrinking particle core model, modified to include a pore diffusivity that decays exponentially. The model solved Eqns. (2.13) - (2.16) numerically. This model was also simplified into equations (2.17) and (2.18).

Figure 4.26 shows how the full model was fit to transient results for four different particle sizes. Parameters used to fit these curves are tabulated in Table 4.10. For the three larger particle size tests shown in the Fig. 4.26, the model gives good correspondence to the

experimental transient. The 0.328 mm particle size is affected by elutriation, which causes the experimental transient to return to background sooner than the model predicts.

Elutriation can be considered in the model through the use of an elutriation time constant, τ_e . To account for elutriation, the batch mass, m_{LS} , in Eqns. (3.54) and (3.55) should be multiplied by $\exp(-t/\tau_e)$. The resulting expressions are:

$$-\frac{dr_{sc}}{dt} = \frac{[SO_2]_I \frac{M_{CaO}}{f_{CaO} \rho_{LS}}}{\frac{3m_{LS}e^{-t/\tau_e}}{Q\rho_{LS}r_p} \frac{r_{sc}^2}{r_p^2} + \frac{1}{h_s} \frac{r_{sc}^2}{r_p^2} + \frac{(r_p - r_{sc})r_{sc}}{D_{es}e^{-t/\tau_p} r_p} + \frac{1}{k_s}} \quad (4.16)$$

$$\frac{[SO_2]_R}{[SO_2]_I} = \frac{1}{1 + \frac{3m_{LS}e^{-t/\tau_e}}{Q\rho_{LS}r_p} \left(\frac{1}{\frac{1}{h_s} + \frac{(r_p - r_{sc})}{D_{es}e^{-t/\tau_p} r_{sc}} + \frac{1}{k_s} \frac{r_p^2}{r_{sc}^2}} \right)} \quad (4.17)$$

Colokyan and Levenspiel [71] give a correlation for the elutriation rate constant which is useful in analyzing the results of these experiments. This correlation is strongly dependent upon the sphericity of the particle, however.

Because of the limits of flow and chemical conditions available when performing testing in a laboratory combustor, analysis of the smaller particles which elutriate is problematic. The low velocities used to eliminate elutriation also result in lower bed temperatures, which inhibit calcination and sulfation. For smaller particles, diffuse interface models may be needed to correctly model behavior in the particle. A diffuse interface model developed by Mantri *et al.* [72] provides a test for the applicability of a shrinking core model vis-à-vis a zone model. Analysis using this model suggests that the shrinking core model is strictly valid for all particle sizes greater than 700 microns if the effective diffusivity does not change. With an exponentially

decaying effective diffusivity, the shrinking core model should be valid for all particle sizes tested in this study.

One reason for the good fit on the remaining transients is that three important model parameters were adjustable. The chemical reaction rate coefficient, k_s , the pore diffusivity, D_{es} and the pore plugging time constant, τ_p , were adjusted to allow the model to fit the data. Values for these parameters are given in Table 4.10. Constant values for these three parameters were found so that multiple transients of varying particle diameter would all fit the model. Normally, fitting a model to curves by adjusting three parameters would not be a sufficient validation of a model. In this case, the simultaneous fitting of several transients, together with supporting particle analysis, assists in substantiating the model.

Two correlations for the film mass transfer coefficient, h_s , were used in the model. The first was a correlation for isolated single spheres given by Froessling [65]:

$$Sh = \frac{h_s d_p}{D_{es}} = 2 + 0.6 Re^{\frac{1}{2}} Sc^{\frac{1}{3}}. \quad (4.18)$$

A similar correlation that is developed specifically for char combustion in bubbling fluidized beds is given by LaNauze [66]:

$$Sh = \frac{h_s d_p}{D_{es}} = 2\varepsilon_b + 0.69 Re^{\frac{1}{2}} Sc^{\frac{1}{3}} \quad (4.19)$$

The value of h_s between the two correlations does not change significantly, but a small change in h_s may require a large change in the value of k_s in order to fit the data. At time zero the core radius equals the particle radius, and Eqn. (2.118) simplifies to:

$$\frac{[SO_2]_O}{[SO_2]_I} = \frac{1}{1 + \frac{3m_{LS}}{Q\rho_{LS}r_p} \left(\frac{h_s k_s}{h_s + k_s} \right)} \quad (4.20)$$

The smaller of h_s and k_s will control sulfation initially. Using the LaNauze or the Froessling correlation, the value of h_s is determined for several particle sizes. Then k_s is adjusted to one number which provides the best fit for the lowest point of the transients. The Froessling correlation resulted in a value for k_s of 1.9 m/s. The values h_s using the LaNauze correlation were greater, and depended on the value of ϵ_b assumed.

The value of k_s could not be evaluated experimentally in a laboratory combustor. Consideration was given to increasing the film mass transfer coefficient to a point where chemistry rather than film mass transfer would control the early reaction. Increasing bed velocity, decreasing particle size, and lowering the bed temperature would all have the effect of increasing the film mass transfer coefficient. Unfortunately, elutriation limited the extent that particle size and bed velocity could be varied. Temperature could not be reduced enough to impact the chemical rate constant without significantly changing the calcination process.

Values for k_s in the literature vary widely. Most investigators [38, 39, 45] base the value on the specific surface area of the limestone, while others base k_s on the area of grains in the particle [50]. The meaning of k_s is strongly attached to the model being used, such that values of k_s must be mathematically backed-out of initial rate data for comparison with shrinking core model k_s values. Sufficient data concerning the parameters used in the tests are not always available in the literature to convert reported values to equivalent shrinking particle core values of k_s .

The value of D_e used in the model fits shown in Fig. 4.26 is 1.7×10^{-6} m²/s. This value is lower than is used in the literature. Hartman and Coughlin [50] use a value of 7.5×10^{-6} m²/s. A larger value of D_e can be accommodated by the model when a value for the maximum local conversion, X_{ml} , is incorporated into the model by multiplying ρ_{CaO} by it in Eqn. (2.120) and ρ_{LS}

by it in Eqns. (2.117) and (2.119). It is valid to add such a term because the increase in volume associated with the sulfation reaction allows only about 50% conversion without growth of the calcine grains [43]. When this addition to the model is made, the value of D_e becomes 3×10^{-6} m²/s, which approaches the larger values found in the literature.

The pore plugging time constant used in the model is empirical. Other methods are available in the literature [50, 51] to account for the decrease in pore diffusivity, but they do not lead to ordinary differential equations and time constants. They also require detailed knowledge of particle parameters such as grain size and surface area. In Fig. 4.26, the value of τ_p is a constant 760 seconds for the four particle sizes.

Analysis using this numerical model highlights the controlling mechanism. For all particle sizes pore-plugging is ultimately the controlling mechanism. There is some mixed control at early times, however. Figure 4.27 shows the values for the resistances to reaction for the four controlling mechanisms for the 0.655 mm particle shown in Fig. 4.26. The time period shown includes the 30 to 90 second time period for which τ_s is analyzed in section 6.3.3. For this smaller particle size, both film diffusion and bed mixing provided a significant resistance to molar flux at the particle surface for early times. Figure 4.27 shows that bed mixing is somewhat more important than film diffusion for the 0.655 mm particle.

Figure 4.28 shows the change in the resistances for a larger, d_p equals 1.85 mm, particle. For larger particles pore plugging is still the ultimate controlling resistance. At early times these large particles also exhibit mixed control, but film diffusion is more significant than bed mixing.

Further refinements to the numerical model are possible. The full model which was used can be converted to a shape-generalized form using Eqns. (2.119) and (2.120) to account for non-spherical particles. It is expected that this model could be refined to handle several classes of particle sizes by adding more equations. Additionally, analysis of the effect of temperature on sulfation has not been done using the full model, but would be fairly simple to do.

Sulfation results compared to model simplifications

Initial validation of the full sulfation model was done by fitting the model solutions to experimental SO_2 transients. Characterization of sulfation can be accomplished more directly, however, by transforming the data into the simplified forms developed in chapter three. The simplified equations were developed by assuming a variety of controlling mechanisms. Comparing the data from the transients to these simplified expressions should give some insight into the nature of sulfation. Four experiments are used to check four controlling mechanisms. These experiments are batch tests with one large (2.58 mm) and one small (0.55 mm) particles size, run at a high (1168 K) and low (1036 K) temperature. These extreme values are used to highlight differences in the controlling mechanism in sulfation.

If sulfation is controlled by the chemical reaction rate, the transient data can be changed into a form indicated by Eqn. (2.127). A log-linear plot of the data should then yield a straight line for early times, with a slope of $1/\tau_{sk}$. In Fig. 4.29 this is done for the four extreme size and temperature experiments. The slope of the function is initially high because of a high reaction rate and a small time constant, but it continuously decreases to a lower slope, indicating lower reaction rates and a longer time constant. The non-linearity of the curve at early times suggests that chemistry is not rate limiting. The curves become straight near the end of the transient, and for the larger particles, the curve is straight for a large portion of the transient, but not the initial portion. This is probably indicative of some other mechanism, which will become more apparent as the other equations are analyzed. It is also important to realize that Eqn. (2.127) is strictly valid only for short times.

Analysis of time constants determined from this function do have some meaning early in the reaction. When taken together, observed activation energies and particle size dependences give additional insight into the controlling mechanism. Since the slope is not constant, measurement of the time constant is dependent upon the time period being analyzed. The time period used for analysis in this study was from 30 to 90 seconds. This time period gives a good indication of the initial reaction rate.

Analysis in chapter three showed that film mass transfer control would result in a constant outlet concentration. This can be seen in Eqn. (2.129). This equation is useful, however, because the initial SO_2 concentration, $[\text{SO}_2]_0$, can provide insight into the initial controlling mechanism. Because the core and particle radii are equal at time zero, diffusion resistance is zero, and the initial outlet concentration is a function of h_s and k_s . Recognizing this, Eqn. (2.120) can be rewritten and expressed as:

$$\frac{[\text{SO}_2]_I}{[\text{SO}_2]_R} - 1 = \frac{2c_2}{d_p} \frac{h_s k_s}{(h_s + k_s)} \quad (4.21)$$

As can be seen in the Froessling and La Nauze correlations [65, 66], Eqns. (4.18) and (4.19), h_s has size dependence of $1/d_p^{1/2}$ to $1/d_p$. By plotting $1/([\text{SO}_2]_I/[\text{SO}_2]_R - 1)$ versus d_p on a log-log plot we can find the size dependence of the function of h_s and k_s . If film mass transfer provides a more significant resistance to reaction than chemistry, the slope should be close to 1.5 to 2. Since there is no size dependence on k_s , a slope close to 1.0 would demonstrate chemistry control.

The results of this analysis are plotted for four particle sizes and six temperatures in Fig. 4.30. The data points are for the minimum $[\text{SO}_2]_R$ during the reaction, since instrument time delay does not allow measurement of $[\text{SO}_2]_0$. Along with the data points, regressions are shown which show an strong consistency. The slopes of the curves are 1.37 ± 0.027 . The slopes of these lines do not appear to have any significant variation with temperature. The lack of temperature dependency, along with a value close to 1.5, supports the notion that film mass transfer provides a more significant resistance to the initial reaction than does chemistry. This also corresponds to analysis using the full model where values of k_s were determined to be somewhat larger than the values of h_s .

If pore diffusion with a constant effective diffusivity is the controlling mechanism, the transients can be plotted according to Eqn. 2.139. Results for the four sample transients are

shown in Fig. 4.31. For the small (0.55 mm) particles the result is a smooth curve with a continuously increasing slope. Figure 4.31 gives the appearance that a line may be drawn to determine τ_{sd} for these small particles at early times. By reducing the scale of the concentration function, however, it is apparent that the curve for these small particles does not yield a straight line at early times. The curve for the 2.58 mm transient shows large fluctuations, but appears to be linear, with a slope of around 1.5, making τ_{sd} equal to 0.667 seconds. From the definition of τ_{sd} in Eqn. (2.139) a value for D_{es} of 3.0×10^{-6} can be computed. This value is close to the value of D_{es} computed from theory-based correlations, and also from the full model if a maximum local concentration of 50% is applied. The linearity of the curve indicates that for larger particles pore diffusion may be controlling. For these particles, a constant diffusivity and a flat plate particle shape assumption give adequate results, at least for the early minutes of the reactions. The other possible explanation for this result is that film mass transfer is significant for larger particle sizes as shown in Fig. 4.31

A final controlling mechanism that needs to be considered is pore-plugging. For sulfation controlled by pore-plugging, the transient should be changed into the form of Eqn. (2.146). Results for the four cases under consideration are shown in Fig. 4.32. For the larger particles, the slope of data in this form is approximately zero, corresponding to an infinite value of τ_p . This correlates with the analysis that gave a straight line slope for the analysis done with a constant value of diffusivity, that is, for pore diffusion control. The smaller particle tests result in fairly straight lines when plotted in this form. The slopes obtained from them correspond to a value of τ_p of roughly 600 seconds. For these smaller particles it appears that pore-plugging controls sulfation from very early times in the reaction.

Examination of the controlling mechanism from these simplified expressions of the transients show a few common features. One is that particle size is a much more significant parameter than temperature. Examination of the figures for these simplified models shows that the major variations in the curve shape are due to differences in particle size. One reason for this is that chemistry is not rate limiting in any of the cases studied. Another common feature of these

analyses is that near the end of the transient the slopes of the curves tend to approach a common constant value. The figures show only the first portion of the transients. In most cases the curves tend to end up with a common slope at the end. For the larger particles this is not quite as apparent since the proximity of the $[\text{SO}_2]_R$ to the background concentration leads to increased fluctuations in the data. This behavior suggests that pore plugging is the ultimate controlling mechanism in sulfation.

In some cases, such as is shown for large and small particles, the controlling mechanism for sulfation is clearly apparent over a large portion of the reaction. For particles sized between those shown, additional analysis must be done. At early times, all of the resistances are involved to some degree, and sometimes no single process dominates. To examine the sulfation reaction over a range of conditions, the effects of particle size, temperature, calcination conditions, and oxygen concentration are considered. Also tests on two other types of limestone are done for comparison with the Gilmore City formation limestone.

Effect of particle size on sulfation

Particle size is a major factor in the sulfation of limestone. The centers of larger particles remain unreacted, so a smaller conversion is achieved. Figure 4.33 shows extents of sulfation for a series of 18 experiments with different particle sizes. As particle size increases, the extent of sulfation decreases. The exception to this is for particles with diameters smaller than approximately 0.3 mm. These particles elutriate from the bed before they have time to react, and this elutriation leads to lower conversions.

As discussed in section two, the sulfation time constant, τ_{sk} , should be proportional to particle radius for sulfation controlled by the chemical reaction rate. Analysis shows that chemistry is not rate limiting. Figure 4.34 plots τ_{sk} versus particle diameter for various temperatures using data plotted in the form of Eqn. (2.127). A regression of the data on this log-log plot gives the size dependence of $\tau_s \propto d_p^{0.28}$. This correlation shows no clear controlling mechanism. One possibility is that bulk mass transfer provides a significant reaction resistance.

As shown in section two, if bulk mass transfer controls the reaction with chemistry as a secondary controlling resistance, the time constant would have no particle size dependence. Another possibility would be that significant pore plugging is taking place, since the pore plugging time constant is assumed to be independent of particle size.

Effect of temperature on sulfation

The temperature effect on the extent of sulfation is shown in Fig. 4.35. This figure plots the extent of sulfation vs. bed temperature for four different particle sizes. The data agree in general with the commonly found result that the optimum temperature for sulfation is 1120 K, although the effect is not nearly as pronounced as is found by other researchers [73]. Lyngfelt and Leckner [73] compared the results of many investigators and found a maximum sulfation conversion closer to 1080 K when using bubbling fluidized bed boilers and laboratory FBC's, and a rapid drop-off of conversion at higher temperatures. They argue that in bubbling fluidized bed boilers, sorbent particles spend a larger percentage of their time in reducing regions. This is due to the location of the coal particles in the emulsion during combustion. The reduction in utilization at higher temperatures is not as drastic in circulating FBC's or when char is used instead of coal for combustion. The laboratory experiments conducted in the present study were done with pre-mixed methane or propane as a fuel. Since reducing conditions do not exist in the emulsion phase of this laboratory FBC, a rapid drop off would not be expected by the theory of Lyngfelt and Leckner [73].

The effect of temperature on the sulfation time constant is seen in the activation energy chart (Fig. 4.36). In this figure the inverse of the sulfation time constant is plotted against the inverse temperature on a log-linear plot. The slope of this curve is proportional to the activation energy, based on an Arrhenius relationship. The values of sulfation activation energy range from 1.73 to 7.33 kcal/mol for limestone tests. These results are all substantially lower than those obtained by Mulligan *et al.* [39], who reported 17.08 kcal/mol and Wen and Ishida [74], who reported 17.48 kcal/mol. Bhatia and Perlmutter [45] analyzed data from Borgwardt [64]. They

obtained an activation energy for chemical rate controlled sulfation of 13.47 kcal/mol, and for product layer diffusion controlled sulfation, an activation energy of 28.7 kcal/mol. Mulligan *et al.* [39] reported a product layer diffusion activation energy of 25.4 kcal/mol.

For chemistry limited sulfation the activation energy would be expected to have values closer to those of the researchers above. For pore diffusion limited catalytic reactions, the observed activation energy takes on a value from 1/2 to 1/4 of the chemical reaction activation energy. In the case of sulfation, however, diffusivity through the pores varies throughout the reaction because the pores get plugged by CaSO_4 as the reaction proceeds. The observed activation energy in this case would indicate the effect of temperature on pore plugging. However, pore diffusion control seems unlikely early in the reaction.

The two most likely reasons for the low activation energies are large resistances by film diffusion or bulk mass transfer. If bulk mass transfer is significant, this could also result in low initial activation energies. As shown in chapter three, bed mixing resistance, together with a secondary chemical reaction resistance, may result in a time constant which is independent of both particle size and k_s . This is especially true in the beginning of the reaction before chemistry and diffusion resistances build up.

For film diffusion control, the activation energy has a low value which corresponds to species transport (1-3 kcal/mol) [52]. The experimental values in Fig. 4.36 are consistent with this range for the smaller particles sizes. The larger particles from these experiments have higher activation energies than the smaller particles. This at first seems counter-intuitive since the smaller particles have higher film mass transfer coefficients, and might be expected to be less dominated by film diffusion. One explanation is that the larger particles are more affected by the calcination process. For the largest particles and the lowest temperatures, the values τ_c and τ_s are approximately equal. The process and degree of calcination and sintering turn out to be very important to sulfation.

Effect of calcination conditions on sulfation

In the shrinking particle core model, the calcination core recedes much more rapidly than does the sulfation core. It might be assumed that the two processes are independent, but this is far from the case. The extent and rate of sulfation will depend greatly on the extent of calcination, and the porosity and surface area developed during calcination. At early times, and particularly at lower temperatures, calcination and sulfation are taking place simultaneously.

In order to investigate how calcination affects sulfation, a series of tests were run with limestone which was calcined in the laboratory combustor in the absence of SO_2 . This lime was then removed from the bed and used in sulfation tests. Figure 4.37 plots the extent of sulfation vs. bed temperature for a 1.55 mm diameter particle size Gilmore City formation limestone under two conditions. In one set the sample had been pre-calcined by batching it into the combustor at $T_{\text{bed}} = 1200 \text{ K}$ with no SO_2 in the bed and extracting the particles after the CO_2 concentration returned to background. The recovered sample was then used for sulfation testing using a batch mass of 17.33 grams, which corresponds to 30 grams of uncalcined limestone. In the other set of experiments 30 grams of 1.55 mm limestone was batched using the normal procedure, which corresponded to the mass after 100% calcination.

The difference between the sulfation of lime and limestone can be seen by examining the extent of sulfation which is achieved for the two processes. Figure 4.31 shows that lime had improved extents of sulfation when compared to the original limestone. If the sample mass had been calculated to account for 80% calcination, as is justified by the calcination results shown in Fig. 4.15, the lime sample mass needed would be larger than 17.33 grams. This would have increased the extent of sulfation above that for limestone even more. At lower temperatures the difference in the extents of sulfation for the two cases is somewhat more pronounced. This is partially explained by the lower extents of calcination for temperatures below 1100 K, as seen in Fig. 4.18.

The effect of sulfation temperature on the lime and limestone sulfation transients is shown in Fig. 4.38. This figure shows the difference in activation energy between the 1.55 mm lime and

limestone particles. The lime particles have an activation energy fairly close to that obtained by Bhatia and Perlmutter [24]. This suggests that sulfation is controlled by the chemical reaction rate at early times for pre-calcined sulfation. The absence of a convective flux of CO_2 from the particle for the lime reaction may result in a higher film mass transfer coefficient. Preliminary calculations for particles of this size suggest that the convective flux of CO_2 away from the limestone particle is greater than the diffusion flux of SO_2 toward the particle for about one calcination time constant at 1123 K. For the larger particles, CO_2 convects away from the particle for longer durations. Figure 4.39 plots the convection flux away from the exterior of the particle vs. time based on the generation rate per particle using CO_2 transients. The resulting curves show that although the peak convective flux away from a particle is about the same for the four sizes, the flux lasts a longer time for the larger particles.

The difficulty with this explanation for lime's increased activation energy is that limestone tends to be more reactive than lime during the first few minutes of a transient. A typical comparison of transient curves for lime and limestone is shown as Fig. 4.40. This curve shows a lower initial reduction in SO_2 for the lime and a slower return to background indicative of a longer sulfation time constant. This lower initial SO_2 reduction and longer time constant were consistently observed in the transients for the five temperatures where lime and limestone performance was compared.

The fact that lime has a higher activation energy, but a lower initial reaction rate than limestone seems somewhat contradictory, but several possible explanations for this behavior exist. One reason might be that limestone may fracture upon batch addition, which would increase the initial surface area for reaction. A second involves the dust that exists on the limestone particles that is not present on the lime particles which have already been through the reactor once. Another reason may be that the assumption of complete calcination in the pre-calcining process is not valid. Finally, sintering of the calcine may give a different response for lime than is seen in the limestone tests. An examination of each of these four hypotheses is warranted in order to determine the reason for the difference in limestone and lime sulfation transients.

Some surface fracturing of the limestone does occur after a batch of limestone is added to the combustor. In the pre-calcination process calcined limestone is removed from the bed and screened to separate it from the sand. Smaller particles of limestone which are roughly the same size as the sand cannot be separated. It is estimated that the unrecovered lime is no more than a few percent of the total mass in the bed after pre-calcination. Additionally, lime may also fracture upon batch addition. The fracturing phenomenon is not considered to be significant enough to give the difference in the sulfation transients that is observed.

The second possible explanation involves dust that is present on the limestone, but is not assumed to be present on the lime. To examine this possibility tests were performed on limestone that was washed in a bucket until the water was no longer cloudy. The limestone was left to dry overnight under a fan. Figure 4.41 shows normalized SO_2 concentration vs. time for washed and unwashed Gilmore City formation limestone with a particle diameter of 2.58 mm. These tests were done with large batches of 150 grams in conjunction with other tests involving extracting particles for particle analysis. The initial reduction in SO_2 concentration is greater for the unwashed limestone. The extent of sulfation for the washed limestone is 82% of the unwashed limestone's extent of sulfation after 110 minutes. This long test period leaves room for error in the background level, however. The difficulty with this hypothesis is that the shape of the profile does not differ between the washed and unwashed limestone. Although the dust on the particles may be a consideration, especially for small particles, it does not appear to be causing the differences in the sulfation between lime and limestone.

A third hypothesis is that the mass used in the lime batches was determined incorrectly, since it assumes complete calcination of limestone. If a lower extent of calcination had taken place in the pre-calcining process, less calcium would be present in the batch than was assumed, and the initial reduction of SO_2 concentration would be lower, as is seen in Fig. 4.41. Along with this, however, lime would have lower extents of sulfation than limestone, which it does not.

A final possible explanation involves sintering of the calcine. Calcination begins at the particle surface where it creates a large surface area consisting of small pores. Sintering begins to

reduce pore surface area as soon as it is formed by calcination. In the case of the limestone addition, sulfur dioxide is present during this process to take advantage of the large surface area before it is reduced by sintering. The other effect of sintering is that in reducing the surface area by collapsing the small pores, the pores that remain are large pores. This has the effect of increasing the accessibility of the reacting species to the unreacted core. In this way larger conversions may take place, but at a slower rate. Particle analysis supports this hypothesis. In Fig. 4.17, the two outer zones of calcine in this particle may be an intermediate region which has been freshly calcined, and an outer region which has been sintered. Overall, sintering seems to be the most plausible explanation for the difference between lime and limestone sulfation transients.

Effect of oxygen concentration on sulfation

Tests were also run to determine the effect of excess oxygen on sulfation of limestone particles. Different approaches have been used in the literature to account for the oxygen concentration. Some include oxygen in the rate equation while others incorporate it into the value of the chemical reaction rate coefficient. Figure 4.42 plots normalized SO_2 concentration vs. time for several batch tests of limestone at different oxygen concentrations. There was no discernible difference in the four transients. This is not unreasonable since there is no indication that the chemical reaction rate is limiting for sulfation under any of the conditions investigated in this study. The effect of oxygen concentration on the chemical reaction rate is therefore not measurable in this analysis.

Results for different limestone types

Figure 4.43 gives a comparison of sulfation transients for 0.655 mm batch tests for the three types of limestone tested. It is apparent that the Cedar Bay #1 limestone seems to give slightly better performance than the Gilmore City limestone, and the Nova Scotia limestone performs considerably worse. This might be expected due to the larger amount of impurities (mainly silicon) in the Nova Scotia limestone, as shown in Table 3.4.

The Nova Scotia limestone consists of 90.5% calcite while the others range from 96 - 98% calcite. This calcium fraction is considered in the analysis for the extent of sulfation. The performance of Nova Scotia limestone is substantially worse even with the lower calcium fraction (f_{CaCO_3}) that is used in Eqn. (3.9). Other researchers [6,2] have investigated limestones containing increased levels of SiO_2 and AlO_3 and found that they actually performed well. The difference is likely to be more attributable to structure than to chemical content. Results comparing the time constants and extents of calcination and sulfation for three limestones are shown in Table 4.11.

Particle Analysis of Sulfated Particles

Particles of limestone reacted for different lengths of time were analyzed with a scanning electron microscope, as well as with polarized and reflected light microscopes. The results from this analysis show a sulfation rim which gets larger with time. Particles extracted at later times show considerable variation in the thickness of their sulfation rims. Typically, the particles that have higher magnesium content, i.e. dolomitic particles, have thicker sulfation rims. Some sample sulfur maps of particles reacted for various times are shown in Fig. 4.44.

The irregular shape to the sulfate rims for the 16-minute and 40-minute samples is due to the structure of the limestone. A significant amount of the power plant limestone consists of oolites with diameters of around 0.5 mm. The sulfate tends to diffuse into the cracks between oolites. This structure is believed to be responsible in part for the size distribution of the limestone as shown in Fig. 3.18. The hypothesis being that the particles tend crack preferentially around the size of the oolites. This causes a lack of particles from 0.5 to 1.5 microns in size. The oolitic structure may also account for the pore diffusion control observed in the larger particles as demonstrated in Fig. 4.31. The interfaces between the oolite and the cementing material may act as large pores which do not plug.

The thickness and profile of the sulfated layers were also determined by microprobe linescans. Particles with layers not affected by oolitic structure were chosen for measurement. Fig. 4.45 shows the results of these linescans. The sulfation layer was seen to have a variety of

thicknesses within a given particle, and also between particles of a given sample. In general, however, samples that had been sulfated for longer times showed thicker layers of sulfate.

The linescans show a ratio of sulfur counts to calcium counts. These represent the mass ratio of sulfur to calcium. The counts ratio is not the same as a mass ratio, however. If these values were converted to molar ratios, they would give molar ratios of S/Ca greater than one. The counts ratio is assumed for this analysis to be proportional to the mass ratio, but not equal to it.

Figure 4.46 shows the relationship between the results of conversion based on transient gas analysis and results computed from the linescans. The solid line is generated by integrating the SO_2 transient from time zero at each point in time. The particle analysis conversion is computed by integrating the local conversion from the linescan data as if the particles were spherical particles of 2.58 mm diameter. The value for the linescan conversion at 80 minutes was multiplied by a factor to make it equal to the conversion based on transient gas analysis. The remaining linescan conversion values are multiplied by the same number so that the results are normalized at the 80 minute transient gas analysis conversion value. Using this method the linescan counts ratio would indicate local conversions of only 28% for the 2 minute sample, increasing to 43% for the sample sulfated for 80 minutes. The small sample size from the linescan data did not allow for a very good match between the particle analysis and gas analysis. The results do show a general consistency of shape between the two transients.

4.2 Boiler tests

Devolatilization

Results from transient tests in the ISU Physical Plant CFB boilers show some differences from results obtained in laboratory-scale combustor tests. Typical is the result shown in Fig. 3.16 for a batch test of 25 lb of 16x18 mesh Illinois wash coal in the CFB boiler. Carbon dioxide concentration rises sharply as volatiles are released from the coal batch and burn. However,

instead of monotonically decreasing to a level characteristic of an extended period of char combustion, the concentration rapidly decays to background levels followed by a brief resurgence in CO_2 levels. These results suggest that char combustion in the CFB boiler is delayed until completion of devolatilization. This delay in char burning until devolatilization is complete is in accordance with observations made by Saxena [1] and Ragland and Weiss [8]. The reason for the differences in char combustion between the laboratory bubbling fluidized bed combustor and the industrial-scale circulating fluidized bed boiler is not clear. Possibly the staged combustion process used in the CFB boiler promotes volatile combustion in the first stage at the expense of char combustion. Only after char reaches the zone of secondary air is sufficient oxygen available to initiate char combustion.

Because devolatilization and char burning do not occur simultaneously in the CFB the contribution of char burning to the CO_2 concentration, $[\text{CO}_2]_f$ is zero. Equation (2.12) is thus modified for the CFB data to be:

$$\frac{[\text{CO}_2]_R}{[\text{CO}_2]_i} = \exp\left(-\frac{t}{\tau_v}\right) \quad (4.22)$$

Total devolatilization times, $t_v = 3\tau_v$, for Illinois washed coal as a function of initial particle diameter, d_p , in the range of 0.925 to 7.12 mm are plotted in Fig. 4.47. A power law dependence upon diameter was evident for all particle sizes. The exponent was calculated to be 0.73 (correlation coefficient 0.527). A lower limit on devolatilization time of 9 s as particles become small was evident for the bubbling bed data and resulted from system lag time. This phenomenon is not seen with the CFB data. The system lag time for the CFB system was calculated as less than one second from step tests of tracer gas, as compared with 3 seconds for the bubbling bed system. Data from boiler tests are more scattered than data from laboratory tests, especially for the larger particles. This is believed to arise from greater uncertainties in carbon dioxide background concentrations.

All data in Fig. 4.47 fall within the 40 % uncertainty band calculated for t_v , except for the largest t_v values measured for particle diameters 2.19, 2.87, and 4.04 mm, and the lowest t_v value for particle diameter 4.04 mm. However, the high and low data points at 2.19, 2.87, and 4.04 mm diameter are approximately equidistant from the regression line. For the largest particles the ratio of the CO_2 peak during devolatilization, $[\text{CO}_2]_i$, compared to the steady state CO_2 background level, $[\text{CO}_2]_{\text{avg}}$, $([\text{CO}_2]_i/[\text{CO}_2]_{\text{avg}})$ is of the same order of magnitude as the residuals.

A power law exponent of 2 indicates heat and/or mass transfer control of devolatilization. The observed power law factor of 0.73 is thought to indicate chemical kinetics plays a role. Chemical kinetics influence would also explain why different coals have different devolatilization times.

Char burning

Both CO_2 profiles and cumulative carbon consumption plots indicate that char burning does not start until the completion of devolatilization. This is in concurrence with Saxena [1] and Ragland and Weiss [8], but disagrees with Christofides and Brown [11], who deduced that devolatilization and char burning occurred simultaneously in a bubbling fluidized bed. Decay of CO_2 concentration to background level prior to rising slightly a few seconds later was the prime indicator of the delay of the beginning of char burnout.

Figure 4.48 compares the results of batch tests of 4x6 mesh Illinois washed coal in the bubbling bed (solid line) and the CFB boiler. In Fig. 4.48 the gradual transition from devolatilization to char burnout for the bubbling bed test of 4x6 mesh coal is clearly seen, while the CFB CO_2 devolatilization goes to the background level prior to rising slightly for char burnout. While a region of char burnout is clearly seen for the bubbling bed profile, it is less distinct for the CFB. This shows that the difference in CO_2 profiles is the result of different combustion dynamics between the bubbling bed and CFB, and not the result of different coal types.

While the ratio $[\text{CO}_2]_f/[\text{CO}_2]_i$ during char burning in the laboratory combustor was as large as 0.5 for the smallest particles, it was never greater than about 0.125 for any batch tests in the CFB boiler. All the combustion air for the bubbling bed enters at to bottom, while the combustion air in the CFB enters in two stages: 50-60% as primary air mainly through nozzles at the bottom of the boiler, and the rest as secondary air at points above the coal injection point. In the range of primary to secondary air flow ratios at which these tests were conducted, no definitive trend could be established regarding influence of air staging upon combustion dynamics because only one sampling point at the cyclone outlet was available.

For short times a plot of $\ln(m(t)/m_i)^{1/3}$ vs. time was a straight line, indicating that the exponential model (Eqn. (2.29)) was valid over these time intervals. Both burning rate per particle and char time constant τ_c were plotted against initial diameter, d_i . Figure 4.49 plots τ_c vs. d_i . The large degree of scatter of τ_c for the two largest particle sizes is believed due to the size of the background fluctuations compared to $[\text{CO}_2]_f$ as well as to the very slow exponential decay of char burnout, which is difficult to accurately calculate in the presence of these fluctuations. A power law relationship for τ_c as a function of diameter gives the exponent of 0.54 with correlation coefficient 0.317. The poor correlation coefficients probably arise from the large fluctuating background for CO_2 concentration.

Christofides and Brown [11] showed that the characteristic time τ_c is representative of the char burning time t_b . The characteristic time will be proportional to d_i^2 for diffusion control and proportional to initial diameter d_i for chemical kinetics control. A power law exponent less than unity indicates other factors are present. Following the analysis of Christofides and Brown [11], the power law found in the present study can be shown to be consistent with fragmentation of particles under chemical rate-limited char combustion. For chemical kinetics control with constant Sherwood number $\tau_c \propto d_i$. Considering char burning under chemical kinetics control with fragmentation, the apparent power law is:

$$\tau_c \propto d_i^{2/3} \cong d_i^{0.67} \quad (4.23)$$

This result, which is in agreement with the experimentally determined power law exponent of 0.54, is suggestive of fragmenting particles under chemical-kinetic control. The highly turbulent environment of a circulating fluidized bed boiler is expected to produce higher mass transfer rates than a bubbling fluidized bed. Furthermore, coal is injected into a region of the boiler where equivalence ratios are less than unity. Accordingly, chemical kinetic control in the boiler is not particularly surprising. The larger characteristic times for char burning in the CFB boiler compared to the laboratory data may also reflect lower oxygen levels in the primary combustion zone of the CFB.

The burning rate calculation is the change in carbon mass per unit time as the particle burns. A log-log plot of burning rate per particle vs. initial diameter is shown in Fig. 4.50. The results of Basu [75], for 4-10 mm particles, are shown for comparison. For this range of particle sizes, this work and the work of Basu [75] are the same order of magnitude. A linear relationship on the log-log scales is clearly evident, indicating a power law relationship between burning rate per particle and initial particle diameter applies. The power law exponent is 2.58 (correlation coefficient 0.965). Basu [75] studied the burning rate of carbon spheres in fluidized bed of sand at 800°C and found a power law exponent of 1.52 to apply. He concluded the burning rate was primarily diffusion controlled for his 4-10 mm particles.

Applying the same analysis for fragmentation as was done for the char time constant and assuming chemical kinetic control, the expected power law exponent is 2.33:

$$dm_c/dt \propto d_i^{7/3} \cong d_i^{2.33} \quad (4.24)$$

This suggests that the burning rate for this work is chemically kinetic controlled with primary fragmentation, in agreement with the analysis of characteristic times for char burning.

Lignite and Nova Scotia coal tests

Due to the limited amount of lignite available for testing, batch sizes were smaller than desired, and the screen size differences wider than desired. The amounts and size ranges tested were: 6.8 kg (15 lb) of 14x20 mesh, 9.4 kg (20.7 lb) of 8x14 mesh, 11.3 kg (25.0 lb) of 4x8 mesh, and 10.5 kg (23.25 lb) of greater than 4 mesh. As noted from Table 3.3, the lignite has considerably more ash, less volatile matter, and less fixed carbon than the Illinois washed coal. Accordingly, it was expected that the devolatilization peak would be smaller and the char burnout even less visible than the Illinois washed coal. Also, the lignite particles were not spherical for any particle size intervals, in contrast to the roughly spherical Illinois washed coal. Although the smallest lignite particles were roughly spherical, those greater than 4 mesh consisted of many long, thin, flat plates. With greater surface area per volume, the particles were expected to devolatilize and burn faster than the more spherical particles which have a smaller surface area to volume ratio.

Figure 4.51 is a plot of the CO₂ concentration vs. time for the 4x8 mesh batch test of lignite. A distinct devolatilization peak is evident, but it is quite small and there is no visible char burnout above the background CO₂ concentration following the devolatilization. With smaller than optimum batch sizes and less volatile matter than the Illinois washed coal (24.16% versus 30.29%) the small devolatilization peak was not surprising. Because there was no distinct evolution of CO₂ above the background level during the expected char region, no calculation of char time constants was possible.

Devolatilization time constants τ_v were calculated and devolatilization times ($3\tau_v$) are plotted vs. initial diameter in Fig. 4.52 along with the results for the Illinois washed coal and Nova Scotia coal. There is a trend for t_v to increase with initial diameter, with power law exponent of 0.423 (correlation coefficient 0.902). This is an excellent correlation, although based on only a limited number of data points. The Illinois washed coal and the lignite have similar t_v .

The Nova Scotia coal tested was a bituminous coal with ultimate and proximate analyses similar to the Illinois washed coal. Tests were run on 18x20, 16x18, 14x16, 10x14 (2), 8x10, 6x8

(2), 4x6 (2) and 1/4x4. The CO₂ profile was very similar to the Illinois washed coal, as was the spectrum at the devolatilization peak. Devolatilization time t_v vs. initial particle diameter is plotted in Fig. 4.52. A power law exponent of 0.49 was found. However, the devolatilization time for the 5.5 mm batch appeared to be suspiciously low. The power law exponent calculated without this point was 0.73, the same as for the Illinois washed coal.

Characteristic char time τ_c for the Nova Scotia coal was also plotted vs. initial particle diameter, Fig. 4.49 along with the characteristic char times for the Illinois washed coal. The trend for the Nova Scotia coal is similar to that for the Illinois washed coal. A power law exponent of 0.74 was obtained, compared to 0.54 for the Illinois washed coal. This result indicates chemical kinetic control with primary fragmentation, as was found for the Illinois washed coal.

Calcination

Several batch calcination tests were run on the ISU power plant boiler, with limited success. CO₂ responses were compared to those for coal batch tests. A small peak was evident, but then the CO₂ concentration was immediately lost in the background fluctuations. Additionally, analysis of calcination requires a faster data acquisition rate than was available during these trials. For these reasons, analysis of calcination was not done on the full scale combustor.

Sulfation

The SO₂ response also suffered from large unsteady fluctuations in the background. Figure 4.53 plots SO₂ vs time for a 100 lb batch of 1.0 mm Gilmore City formation limestone. The background level is shown as a straight line, which was determined by averaging the SO₂ readings for the first 20 minutes. The large fluctuations of $\pm 25\%$ of the background level are believed to be caused by the unsteady coal feed. The mass of coal is intermittent because drag conveyors in the feed system provide an unsteady release of coal into the feed tubes. The SO₂ released from the coal is believed to follow this irregular pattern. Near the end of the transient

there is an unexplained rise in the SO_2 concentration. This type of unpredictable behavior in the transient is common. It is unclear whether any long-period changes in the SO_2 background level are occurring over the course of the reaction. Regression analysis of the SO_2 concentration for the first 20 minutes of data results in a downward slope, which makes the increase in SO_2 level at the end of the experiment even less explainable. The results shown in Figure 4.53 represent the best of the experiments run at the power plant.

Figure 4.54 compares the results of full scale boiler testing to a test in the laboratory FBC. The full scale test used 1.00 mm limestone, while the mean size of the limestone in the laboratory FBC was 0.925 mm. The results are similar because the ratio of limestone mass to volumetric air flow between the two cases is similar. The results are not expected to correspond exactly since the operating conditions are not the same. Figure 4.54 shows that the response of the full-scale boiler is similar to that observed in the laboratory.

In Fig. 4.55 the normalized SO_2 difference data is plotted on a log-linear plot to determine sulfation time constants. Results from the full-scale boiler appear to "straddle" the curve from the laboratory experiment for much of the curve, which suggests that the sulfation process in the full-scale boiler may actually be similar to that observed in the laboratory FBC. Nevertheless, calculation of time constants from the full-scale boiler using the slope of the response curve was not performed for several reasons.

First, the circulating bed may not behave like a CSTR. Although there is significant mixing of the solid particles, a gradient in $[\text{SO}_2]_R$ along the height of the combustor may be significant. Another consideration is that the use of primary and secondary air results in regions near the bottom of the bed where reducing conditions exist. Calcium sulfide formation may occur instead of CaSO_4 in this region. CaS does not have the high molar volume that CaSO_4 has and may penetrate into the particle. A final consideration is that much of the limestone in the full scale unit is smaller than was analyzed in the lab scale FBC. Thus chemistry control for the early portion of the transient is more likely. More detailed consideration of elutriation and cyclone efficiency is necessary for this analysis. Additionally, a diffuse interface model may be useful for

the small particle sizes present in the full-scale boiler.

Particle analysis of particles extracted from full-scale boiler

In Fig. 4.56, SEM sulfur maps from power plant bottom ash show a sulfate rim similar to that which was seen in the samples from laboratory experiments. This suggests that the sulfidation reaction is not of major importance in the full scale circulating FBC. Chemical analysis of FBC ash from the ISU physical plant has been conducted by Dawson *et al.* [76] in a study of the feasibility of controlling ash chemical content for further use in cement. Table 4.12 was extracted from that study. This table shows that larger bottom ash particles have a lower percentage of SO_3 , a higher percentage of SiO_2 , and a higher loss on ignition (LOI).

The larger percentage of CaO in the larger particles is balanced to some degree by the increased LOI, which is the weight percent of CO_2 driven off prior to the analysis. The higher LOI gives some evidence of a lower extent of calcination for the larger particles. The particle size effect on sulfation, as determined by the fraction of SO_3 , is similar to that observed in the lab. The probable cause for this is limited penetration of SO_2 into the particle resulting in sulfate rims as seen in the particle maps. The larger particles have a larger unreacted CaO core.

4.3 Spectral analysis

Laboratory scale bubbling fluidized bed

Spectral analysis was developed as a new method to analyze the CO_2 concentration data and calculate the devolatilization and char time constants. Figure 4.57 is a Bode plot of a batch test in the bubbling bed laboratory combustor test of 5g of 14x16 coal. This Bode plot is consistent with a dynamic system consisting of two linear processes in parallel (devolatilization and char burning).

This plot supports the validity of the combustion model of Eqn. (2.29) with the two concurrent exponential decays. The cornering frequencies as shown give $\tau_v = 3.4$, and $\tau_c = 75.0$. These values differ from values calculated in the time domain by only 6%.

Figures 4.58 and 4.59 plot the devolatilization times, t_v , and char time constants, τ_c , vs. initial diameter, respectively for the bubbling fluidized bed data as calculated using spectral analysis. Also plotted on these figures are the linear regression lines for t_v and τ_c calculated using time domain methods. As was previously noted for the time domain analysis, the devolatilization time for diameters less than 3.0 mm are independent of diameter, and are constrained by the system lag time, τ_l . For initial particle diameters less than 4 mm, there seems to be good correlation between the spectral analysis and time domain calculations. At larger diameters the time constants calculated with spectral methods are only about 2/3 of the time domain values.

The char time constants calculated with spectral methods correspond fairly well with time domain methods for diameters less than about 2 mm, but fall further below the time domain values as diameter increases. Spectral analysis is limited in that a data set of minimum length must be taken before performing spectral analysis, or erroneous results can be obtained. For the bubbling bed tests of this work all tests were approximately 2-3 minutes in length, which is adequate for time domain analysis. The time interval for the smallest particles was adequate for proper spectral analysis, but proved too short for larger particles.

Figure 4.60 is a Bode plot of a 5g 6x7 mesh coal batch test in the bubbling bed combustor. From the cornering frequencies, $\tau_v = 2.9$ (compared to 2.69 from time domain analysis) and $\tau_c = 177$ (compared to 238 from time domain analysis). This clearly shows that despite the distinct cornering frequencies, the char time constant calculated is significantly less than that calculated from time domain analysis. Because the length of the data for this test of larger particles was not long enough, time constants are smaller than expected based on time domain values, even though distinct cornering frequencies are seen on the Bode plot.

In general, sSpectral analysis of batch tests were not as successful as the example of Fig. 4.60 because not all data sets had an adequate length to ensure proper determination of τ_c .

However, the results obtained in this work demonstrate that spectral analysis will yield results comparable to time domain results when the data set time length is adequate.

Industrial scale CFB boiler

The CFB boiler batch test data were analyzed using spectral methods in the same manner as the laboratory scale combustor data. Figure 4.61 is a typical Bode plot for a 25 lb batch test of 14x16 mesh coal. There is an excessive amount of "noise" at the higher frequencies due to the background fluctuations. Because of this the transition from horizontal to the -20dB/decade slope of devolatilization region is very difficult to observe. From the asymptotes of Fig. 4.61 $\tau_v = 3.2$ (compared to 5.97 for time domain analysis) and $\tau_c = 526$ (compared to 987 for time domain analysis). It is believed the high frequency fluctuations and shorter than optimum time interval are primarily responsible for the low characteristic times calculated from spectral analysis.

Digital filtering, windowing, and averaging techniques were unsuccessful in reducing the noise to improve the visibility of the cornering frequency. Because the effects of the background fluctuations could not be removed from the analysis, meaningful analysis of the CFB boiler data using spectral analysis was not possible. Had the background fluctuations been more ergodic, it is believed spectral analysis would have been as successful with the CFB data as with the bubbling bed data. This Bode plot is consistent with a dynamic system consisting of two linear processes in series.

5. CONCLUSIONS

5.1 Laboratory reactor testing

Devolatilization

The estimates of devolatilization time for particles larger than 3 mm approach devolatilization times predicted by Essenhig's [6] relationship, but are 6-40 % larger than those predicted by Ragland and Weiss' [8] relationship. The instruments used in this work did not allow the measurement of devolatilization times smaller than about 9 s due to a significant lag in the sampling system, although, in principle, faster times could be measured with appropriate instrumentation.

Char combustion

The exponent for the power law describing τ_c and t_c vs. d_i is only 1.33 whereas mass transfer-limited char combustion predicts an exponent between 1.5 and 2.0. The hypothesis of intrinsic chemical kinetics being rate limiting was not supported by the data or additional tests. The Indiana bituminous coal used in these tests fragmented during volatiles release resulting in fragments that burned much faster than the original particles. It is hypothesized that primary fragmentation, which is thought to increase with initial particle diameter of coal particles, is responsible for the smaller than expected exponent in the power law for char burning. Char fragments recovered from the bed immediately after devolatilization support this hypothesis. These results highlight the importance of fragmentation in understanding burning rates under realistic combustion conditions.

Calcination

Calcination is largely controlled by the chemical reaction rate. This is demonstrated by the agreement in activation energies with previous literature for chemistry-rate-controlled calcination.

The size dependence for the calcination time constant was greater than one. Size dependence increases as temperature increases. This is shown by reduced activation energies. Particles were tested under isothermal conditions and it is assumed that heat transfer is not limiting in this reaction. However, when a large sample mass is used a greater drop in temperature occurs, and the observed reaction time is longer. Temperature appears to have little effect on the extent of calcination, except at low temperatures and with large particles. In most cases the extent of calcination was close to 80%.

The chemical reaction rate is a function of the partial pressure and equilibrium partial pressure. This is apparent from the slight change in the calcination time constant with increasing inlet CO_2 concentration. The calcination time constant is inversely proportional to the difference between the equilibrium concentration and the inlet concentration. Calcination is not controlled by film diffusion. Samples reacted at different gas velocities showed little difference in calcination time constants.

The shrinking core model for calcination describes the mechanisms involved in calcination. Although validation of the full scale model needs to be done using a numerical solution, the simplified equations generated by the model help to explain calcination. The use of transient gas analysis is useful to observe how pore diffusion may play a role in calcination of larger particles at higher temperatures. The ability to validate this mechanism in an actual combustion environment is an improvement to existing laboratory procedures.

There are indications of a loss of surface area during the calcination process as suggested by the literature [28-30]. This sintering phenomenon is shown in particle analysis by two distinct CaO rims around some of the particles. Surface area loss may present itself by an increased sulfation reaction rate early in the transient, when the outer edge of the particle is undergoing calcination. Surface area testing shows that at higher temperatures, surface area and pore volume are reduced. The mean pore diameter is greater for Gilmore City formation limestone when calcined at higher temperatures. SEM and reflected light photographs show a possible change in structure over the radius of a particle after reacting for 2 minutes in a 150 gram batch addition of

2.58 mm limestone.

Sulfation

The sulfation reaction is dependent upon the type of limestone in use and its properties after calcination. The limestone used in this study exhibited a sulfation layer around a shrinking unreacted particle core. Testing in laboratory conditions revealed pore plugging as the dominant controlling mechanism for sulfation of the Gilmore City formation limestone. At early times, however, external mass transfer provided a significant resistance to reaction in the fluidized bed combustor. The reaction was not controlled by the chemical reaction rate at any condition tested in the laboratory scale FBC. This is due in large part to the limitations on particle size that can be examined in the bubbling bed before particles are entrained. Had operating conditions allowed for reaction of smaller particles without elutriation, the chemical reaction resistance may have been more substantial. For larger particles pore plugging is delayed, possibly due to the existence of larger pores and cracks in the larger oolitic particles. Grain-level product layer diffusion resistance was not included in the model that was used in this study. The existence of an unreacted particle core supports the conclusion that pore plugging and not product layer diffusion is the major controlling mechanism.

Temperature did not have a large influence on the extent of sulfation in this study. There may be a small peak in the extent of sulfation at approximately 1123 K, but it is much less pronounced than is reported in the literature [22,73]. Part of this may be the lack of a reducing region in the emulsion phase, as exists in coal combustion [73].

No clear controlling mechanism can be deduced from the relationship between the sulfation time constant and the particle diameter. A power relationship of 1.0 would indicate chemistry control and a larger value may indicate pore diffusion control. The value of 0.28 for the power relationship indicates that pore-plugging, film diffusion and bulk mass transfer all may contribute to the reaction resistance early in the reaction. Activation energy analysis for early times supports film diffusion, bulk mass transfer, and pore plugging as possible significant

resistances early in the reaction.

Analysis of two other limestones showed a better sulfation performance for the Cedar Bay #1 limestone when compared to the Gilmore City limestone and a considerably worse performance for the Nova Scotia limestone. The reduction in the extent of sulfation for the Nova Scotia limestone was more than could be accounted for by the smaller amount of CaCO_3 in its chemistry. The reduction in performance for this high SiO_2 content limestone is in contradiction to the findings of Mulligan *et al.* [39] and Dam-Johansen and Ostergaard [35].

Overall, modeling sulfation as a shrinking core with decaying diffusivity well describes the results seen in the laboratory. The model can be fit with reasonable values for effective diffusivity and chemical reaction rate constant to effectively simulate the gas transient which results from a batch test. Moreover, simplifications of the model show that transient gas analysis is an effective means for determining the controlling mechanism in sulfation and for characterizing the reaction.

5.2 Circulating fluidized bed boiler testing

The FTIR is a powerful tool for studying coal combustion processes in an on-line CFB boiler, without interrupting the boiler processes. It has been shown that the characterization of coal can be studied on-line during normal operation. However, lack of control over boiler functions, such as air flow and bed temperature, make it difficult to vary these parameters and evaluate with confidence their affects on the combustion process. The present study, though, found no evidence that they affected the results.

The CFB boiler combustion dynamics are very complex, even more so than in the bubbling fluidized bed combustor. It is believed that staged combustion has an influence on some of the parameters studied here, but the specific impact could not be studied due to the limitation of having only one sampling point at the cyclone outlet.

Better calculation of τ_v and τ_c could be obtained if smoother steady-state flow of coal could be attained in the CFB boiler. Coal tended to pile-up against cleats on the coal-feed conveyor, producing a noisy CO_2 background that interfered with signal analysis.

The small volume of the gas cell used with the FTIR system made possible the study of fast combustion dynamics, but decreased the resolution and detection of trace species (such as HCl and H₂S). Use of a longer path length cell to improve detection of such gases would diminish the system's utility to study rapid transients.

While CO and methane were present during devolatilization of every test in the bubbling bed combustor, they were present only for tests of smaller particle sizes in the CFB and the amounts were less than those seen in the bubbling bed. The presence of CO and methane indicated oxygen starvation occurred during devolatilization, at least locally to the particles. Contrary to laboratory studies, char burnout did not begin until devolatilization was complete in the power plant tests. This result is in agreement with other authors, such as Saxena [1] and Ragland and Weiss [8] who theorized char combustion did not begin until devolatilization was complete.

The devolatilization time was found to be proportional to $d_p^{0.73}$. Char burnout dynamics differed significantly from those seen in the bubbling bed. Contrary to Christofides and Brown [11] who suggested devolatilization and char burning occurred simultaneously in the bubbling bed, the CO₂ profiles in the CFB boiler indicated that char burning did not commence until a short time after the completion of devolatilization. The char time constant was proportional to $d_p^{0.54}$, or $d_p^{0.55}$, depending on the method used to calculate it. This suggests the char combustion is controlled by chemical kinetics with primary fragmentation.

Theory would indicate that the char time constant would be equal to 2 for diffusion control, and 1 for chemical kinetics control. With the much higher flow velocities in the CFB boiler and coal injected into an oxygen-lean region of the boiler, it is possible that chemical kinetics control might dominate, rather than diffusion.

The burning rate of single particles was also studied. The burning rate determined in the CFB by this work is the same order of magnitude as reported by Basu [73]. The burning rate is expected to be proportional to d_p for diffusion control, and d_p^2 for chemical kinetics control. This

work found the burning rate to be proportional to $d_i^{2.58}$, again indicating chemical kinetics control with primary diffusion.

Sulfation

Full scale tests at the Iowa State University (ISU) power plant highlight the difficulties in using transient gas analysis at full scale units, but show similarities to the results obtained in the lab. The large fluctuations associated with the coal feed system makes obtaining a steady background concentration extremely difficult. Interpretation in the midst of large fluctuations is also unreliable when analyzing time-series data.

Spectral analysis was not used in the calcination or sulfation analyses as had been hoped for two reasons. The non-linear nature of the sulfation reaction does not allow for interpretation of the frequency plots. Furthermore, the large amount of correlated noise masks the signals of interest. It is hoped that some method similar to spectral analysis can be developed to characterize sorbent reactions. The use of time series data developed from batch tests does lend itself to use in the full scale, however.

5.3 Spectral analysis

Spectral analysis was developed as a powerful new method of determining char and devolatilization time constants from the transient CO_2 emissions from coal combustion. The Bode plot obtained from spectral analysis was consistent with the assumption of rapid exponential devolatilization decay and slower exponential CO_2 decay during char burning, at least for the bubbling bed data. Horizontal and -20 dB/decade straight line asymptotes fitted to the Bode plot provided two distinct cornering frequencies, corresponding to devolatilization and char time constants. Distinct cornering frequencies representing the reciprocals of τ_v and $\tau_c/3$ were observed. However, it was shown that a data set of minimum time length must be recorded for use with spectral analysis to prevent getting falsely low time constants.

For the bubbling bed combustor the time constants calculated with spectral analysis were in good agreement with those calculated using time domain methods for smaller particle sizes, where the time length of the data set was adequate. However, it was found that the time constants calculated with spectral analysis were consistently smaller than those calculated with time domain methods for the larger particle sizes, indicating the lengths of the data sets were too short. Some order of magnitude estimate of the char time constant must be known before taking data to ensure taking data for a long enough time period for spectral analysis to be effective. The background fluctuations in the CFB CO₂ data precluded its use for spectral analysis, as the "noise" introduced by the high frequency background fluctuations masked the actual spectral features.

5.4 Population balance

In many studies, the effects of particle distributions have been largely ignored. This study suggests that particle distributions, even narrow distributions, significantly affect the transient response of coal combustion in a fluidized bed. Furthermore, this study represents a unified theory that explains the wide differences observed between the impulse responses of small and large particles.

While a solution to the population balance equation goes a long way towards modeling char combustion phenomena, it is only a first step. For small particles, this model can be refined by including terms for chemical kinetics, attrition, and oxygen depletion. For large particles, future work should address fragmentation distributions. Indeed, with a solution for an arbitrary particle distribution, it may be possible to ascertain the degree of fragmentation by examining curvature characteristics of transient responses.

In contrast with models for char combustion, satisfactory models for volatile combustion transients remain elusive. In this study, the CO₂ measurement system was too sluggish to adequately track volatile transients in the size range studied.

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TABLES

Table 2.1 Summary of char burning regimes

Regime	n	a_0	$(t_c - t_i)/(\tau_c - \tau_i)$	CO ₂ Profile	Expected power law for burnout time
Film Diffusion (fixed Sh No. = α)	2	αD_m	1/2	$(1-at)^{1/2}$	d^2
Film Diffusion with (var. Sh No. = $\beta d^{1/2}$)	3/2	βD_m	2/3	$(1-at)$	$d^{1.5}$
Intrinsic chemical kinetics	1	k_0	1	$(1-at)^2$	$d^{1.0}$

Table 3.1 Gas analyzer equipment and associated accuracies

Gas	Analyzer	Scale	Drift (on a 24 hour basis)	Calibration gas	Repeatability
O ₂	Beckman 755 O ₂ analyzer	25%	1% of full scale	8.10% O ₂ in nitrogen	1% of full scale
CO ₂	Beckman 870 CO ₂ analyzer	20%	1% of full scale	15.0% CO ₂ in nitrogen	1% of full scale
CO	Beckman 870 CO analyzer	1.2%	1% of full scale	0.80% CO in nitrogen	1% of full scale
NO _x	Horiba VIA-300 NO _x analyzer	1000 ppm	1% of full scale	800 ppm in nitrogen	1% of full scale
SO ₂	Horiba VIA-500 SO ₂ analyzer	2000 ppm	1% of full scale	1490 ppm SO ₂ in nitrogen	1% of full scale

Table 3.2 Spectral Ranges for FTIR calibration

GAS	RANGE (cm ⁻¹)
CO ₂	767.0 - 736.0
SO ₂	1368.2 - 1342.2
CO	2186.6 - 2133.9
NO ₂	1612.3 - 1582.0
NO	1919.0 - 1837.0
N ₂ O	1259.0 - 1248.0

Table 3.3 Coal analyses

Proximate Analysis %

SAMPLE	MOISTURE	ASH	VOLATILE MATTER	FIXED CARBON
Illinois washed coal	3.84	18.67	30.29	47.20
	0.00	19.41	31.50	49.09
Indiana bituminous	13.86	8.02	33.05	45.07
	0.00	9.31	38.37	52.32
Kentucky coal	6.05	17.24	33.69	43.02
	0.00	18.35	35.86	45.79
Lignite	34.45	30.20	24.16	11.19
	0.00	46.07	36.86	17.07
Nova Scotia coal	4.81	21.31	28.21	45.67
	0.00	22.39	29.64	47.97

Ultimate Analysis %

SAMPLE	SULFUR	C	H	N	O
Illinois washed coal	3.16	61.95	4.07	1.05	11.10
	3.29	64.42	3.79	1.09	8.00
Indiana bituminous	1.85	73.84	5.13	1.12	8.76
	2.03	81.40	5.66	1.23	9.66
Kentucky coal	2.82	61.21	4.43	0.97	13.95
	3.00	65.15	3.99	1.03	7.45
Lignite	0.38	24.38	2.36	0.20	42.48
	0.58	37.19	2.28	0.31	13.57
Nova Scotia coal	4.57	57.62	3.79	0.81	11.90
	4.80	60.53	3.42	0.85	8.01

Table 3.4 Chemical analysis of limestones used

	Gilmore City Formation 1993	Gilmore City Formation 1995, Dp = 1.85 mm	Gilmore City Formation, 1995, Dp = 0.328 mm	Cedar Bay #1, Nova Scotia, 1995 Dp = .55 mm	Nova Scotia, 1995 Dp = 0.55 mm
SrO		0.02	0.02	0.07	0.03
MgO	1.15	0.78	0.42	0.35	0.52
Fe ₂ O ₃	0.24	0.21	0.15	0.01	0.27
K ₂ O	0.01	0.02	0.02	0.01	0.24
SO ₃	0.56	0.01	0.01	0.03	0.04
TiO ₂	0.03	0.01	0.01	0.01	0.05
MnO	0.01	0.02	0.02	0.01	0.07
SiO ₂	1.17	0.96	0.34	0.13	4.17
CaO	53.86	54.00	55.12	54.72	50.71
P ₂ O ₅	0.06	0.01	00.00	0.01	0.01
Al ₂ O ₃	0.60	0.06	0.07	0.07	0.98
Sum	57.69	56.10	56.18	55.42	57.09
% calcite	96.17	96.42	98.42	97.71	90.55

Table 4.1 Variable temperature tests with 1.55 mm Indiana coal

Test	Temperature (K)	τ_c (s)	t_c (s)
BTa1	1039	130	93
BTa2	1049	128	104
BTa3	1082	155	109
BTa4	1100	156	106
BTa5	1143	185	120

Table 4.2 Averaged ratios of $(t_c - t_i)/(\tau_c - \tau_i)$ for Indiana coal

d_i (mm)	$t_c - t_i$ (s)	$\tau_c - \tau_i$ (s)	$(t_c - t_i)/(\tau_c - \tau_i)$
0.66	28	66	0.45
0.78	43	75	0.58
0.93	53	109	0.49
1.02	69	75	0.91
1.02	56	84	0.66
1.26	74	119	0.62
1.48	95	154	0.62
1.86	137	194	0.69
2.65	171	271	0.63
2.84	268	339	0.79
3.33	290	452	0.64
4.38	276	801	0.34
5.18	378	969	0.39
6.15	269	930	0.29

Table 4.3 Mass fractions for uniform λ distributions

Mesh	$d_{\max}$ (mm)	$d_{\min}$ (mm)	Δd (mm)	ϕ_o^1	ϕ_o^2	ϕ_o^3	ϕ_o^4
16x18	1.18	1.00	0.18	1.00	0.55	0.38	0.31
18x20	1.00	0.85	0.15		0.45	0.32	0.26
20x25	0.85	0.71	0.14			0.30	0.24
25x30	0.71	0.60	0.11				0.19

Table 4.4 Impulse response data

Mesh Designation	16x18	16x20	16x25	16x30
Sieve Data				
$d_{\min}$ (mm)	1.00	0.85	0.71	0.60
$d_{\max}$ (mm)	1.18	1.18	1.18	1.18
Simplex Est.				
$d_{\min}$ (mm)	0.89	0.83	0.77	0.68
f (mm ² /s)	0.0091	0.0010	0.0100	0.0104
ϕ (g/mm)	6.19	5.26	4.53	3.67
t_i (s)	43.5	34.3	29.6	22.2

Table 4.5 Power-law for dependence of τ_c on particle size as a function of temperature. ($U_o = 1.12$ m/s, $[\text{CO}_2]_i$ varies with temperature, $m_{LS} = 30$ g. Tests at 1123 K were conducted with $m_{LS} = 20$ g and in the absence of SO_2 injection.)

Bed temperature, K	Power law exponent
1035	0.91
1067	1.20
1094	1.31
1123	1.04
1124	1.44
1151	1.42
1168	1.40
1193	1.62

Table 4.6 Calcination activation energies for various particle sizes. ($U_o = 1.12$ m/s, $[\text{CO}_2]_i$ varies with temperature, $m_{LS} = 30$ g. Tests done with $d_p = 1.28$ mm were conducted in the absence of SO_2 injection.)

Particle diameter, mm	Activation energy, kcal/mol	90% confidence limits for activation energy, kcal/mol
0.550	43.4	± 6.09
0.925	45.5	± 7.94
1.28	39.4	± 3.05
1.55	38.6	± 9.11
2.58	29.5	± 7.45

Table 4.7 Calcination time constant for various background CO_2 concentrations. ($m_{LS} = 25$ g. of Gilmore City formation limestone, $d_p = 1.29$ mm, $U_o = 1.5$ m/s, $T_{bed} = 1123$ K)

$[\text{CO}_2]_i$ (%)	$[\text{CO}_2]_E - [\text{CO}_2]_i$ (mol/m ³)	τ_c (s)
7.78	4.36	28.2
10.23	4.10	30.3
12.16	3.89	36.5
15.10	3.57	34.1
17.48	3.31	38.7

Table 4.8 Effect of superficial velocity on calcination time constant and extent of calcination. (Gilmore City limestone, $d_p = 1.55$ mm, $m_{LS} = 30$ g., $T_{bed} = 1123$ K)

Superficial velocity (m/s)	$[\text{CO}_2]$ background (%)	τ_c (seconds)
0.95	7.95	32.9
1.19	6.96	32.9
1.43	6.48	30.7
1.66	6.12	42.1
1.92	5.92	31.3

Table 4.9 Time constants and reaction extents for two limestone types with various particle sizes. ($T_{bed} = 1123$ K, $U_o = 1.1$ m/s, $m_{LS} = 20$ g.)

	Mean particle diameter (mm)	τ_c (s)	Extent of Calcination (%)
Cedar Bay #1	0.231	4.59	92.8
	0.328	4.95	75.8
	0.463	5.02	77.8
	0.655	8.73	80.3
	0.925	12.3	85.3
Nova Scotia	0.328	4.17	75.4
	0.463	9.83	84.4
	0.655	11.0	88.7

Table 4.10 Parameters used in model for Figure 4.26. (Gilmore City limestone, $m_{LS} = 20$ g., $T_{bed} = 1123$ K, $U_o = 1$ m/s)

Parameter	Value	Method of determination
k_s	1.9 m/s	fit (depends on h_s correlation used)
D_{es}	1.7×10^{-6} m ² /s	fit
τ_p	760.0 s	fit
h_s	0.53 m/s (0.925 mm)	Froessling correlation

Table 4.11 Time constants and reaction extents for three limestone types with various particle sizes. ($T_{\text{bed}} = 1123 \text{ K}$, $U_o = 1.1 \text{ m/s}$, $m_{\text{LS}} = 20 \text{ g.}$)

	Mean particle diameter (mm)	τ_c (s)	Extent of Calcination (%)	τ_s (s)	Extent of Sulfation (%)
Cedar Bay #1	0.231	4.59	92.8	58.8	30.2
	0.328	4.95	75.8	89.8	32.4
	0.463	5.02	77.8	91.1	31.0
	0.655	8.73	80.3	99.5	28.2
	0.925	12.3	85.3	128.	21.5
Nova Scotia	0.328	4.17	75.4	56.8	21.4
	0.463	9.83	84.4	69.7	17.0
	0.655	11.0	88.7	65.8	13.2
Gilmore City	0.165			21.14	8.02
	0.196			30.96	14.24
	0.231			43.08	25.05
	0.275			68.26	31.49
	0.328			76.09	31.18
	0.390			84.32	30.22
	0.463			95.04	26.86
	0.550			95.08	25.76
	0.655			94.08	23.10
	0.780			104.93	21.60
	0.925			105.90	17.67
	1.090			106.62	17.03
	1.290			110.09	15.57
	1.850			128.00	11.07
	2.580			168.85	7.71
	3.075			121.87	7.66
	3.675			156.07	5.69

Table 4.12 X-ray fluorescence chemical analysis of ISU boiler ash. [76]

	Bag house Ash	Bottom Ash	Bottom Ash (+12)	Bottom Ash (12x20)	Bottom Ash (20x60)	Bottom Ash (60x100)	Bottom Ash (- 100)
SiO ₂	33.39	9.83	11.07	11.01	9.73	6.76	7.01
Al ₂ O ₃	15.22	3.01	3.14	3.44	3.01	1.68	2.12
Fe ₂ O ₃	8.21	1.23	1.65	1.36	1.04	1.04	2.08
MgO	0.61	0.50	0.56	0.56	0.46	0.37	0.42
CaO	20.92	58.94	65.58	64.01	57.61	57.20	55.00
Na ₂ O	0.00	0.00	0.27	0.27	0.00	0.19	0.00
K ₂ O	1.56	0.27	0.35	0.39	0.35	0.14	0.06
TiO ₂	0.84	0.17	0.18	0.17	0.14	0.12	0.22
P ₂ O ₅	0.08	0.04	0.05	0.03	0.03	0.03	0.03
SO ₃	8.26	27.49	8.58	15.49	30.05	37.16	37.49
SrO	0.08	0.07	0.07	0.07	0.08	0.08	0.08
BaO	0.03	0.00	0.00	0.00	0.00	0.00	0.00
LOI	10.90	3.00	10.00	4.30	1.30	0.60	0.40
Total	100.11	104.54	101.51	101.10	103.81	105.36	104.89

FIGURES

Fig. 2.1 Schematic of the shrinking grain core model

Figure 2.2: Block diagram of system impulse input $u(t)$ and the response to it $y(t)$

Figure 3.1 Schematic of laboratory combustor and instrumentation

Figure 3.2 CO₂ profile for batch test of 5 g of 7x8 mesh Kentucky coal in bubbling fluidized bed combustor

Figure 3.3 CO₂ transient. ($T = 1124\text{ K}$, $U_o = 1.12\text{ m/s}$, $m_{LS} = 30\text{ g}$, $d_p = 0.55\text{ mm}$, $O_2 = 5.0\%$, Gilmore City formation limestone, $[SO_2]_i = 1478\text{ ppm}$)

Figure 3.4 SO₂ transient. ($T = 1124\text{ K}$, $U_o = 1.12\text{ m/s}$, $m_{L,S} = 30\text{ g}$, $d_p = 0.55\text{ mm}$, $O_2 = 5.0\%$, Gilmore City formation limestone, $[CO_2]_i = 8.4\%$)

Figure 3.5 Ahlstrom Pyropower circulating fluidized bed boiler schematic

Figure 3.6 Rapid dump coal hopper used on CFB boiler coal drag conveyor

Figure 3.7 Primary to secondary air flow rate vs. coal flow and total air flow rate vs. coal flow in the CFB boiler

Figure 3.8 FTIR system

Figure 3.9 Boiler sample probe and filtration system

Figure 3.10 Typical FTIR background spectrum

Figure 3.1.1. Schematic of Michelson interferometer

Figure 3.12 Typical interferogram

Figure 3.13 Schematic of White gas cell

Figure 3.14 Typical predicted value vs. actual value plot for CO from QUANTIR for calibration method

Figure 3.15 Six gas reference spectrum

Figure 3.16 CO₂ profile from batch test of 25 lb of 16x18 mesh Illinois washed coal in the CFB boiler

Figure 3.17 Cumulative carbon consumption plot for batch test of 25 lb of 16x18 mesh Illinois washed coal in CFB boiler

Figure 3.18 Size distribution of ISU power plant (Gilmore City formation) limestone

Figure 4.1 CO₂ profile for batch test of 5 g of 7x8 mesh Kentucky coal in bubbling fluidized bed combustor

Figure 4.2 t_v vs. coal particle diameter

Figure 4.3 ($\tau_c - \tau_i$) vs. coal particle diameter

Figure 4.4 Inverse characteristic burnout times versus inverse bed temperature for 1.55-mm Indiana coal

Figure 4.5 Particle distribution of Indiana char after primary fragmentation

Figure 4.6 Typical small particle response

Figure 4.7 Small particle char model (16x20 mesh)

Figure 4.8 Small particle char model (16x30 mesh)

Figure 4.9 Cumulative weight distribution

Figure 4.10 Estimated initial λ distribution

Figure 4.11 Large particle char model (3.5x4 mesh)

Figure 4.12 Comparison of calcination model to transients. ($T_{\text{bed}} = 1123 \text{ K}$, $m_{\text{LS}} = 30 \text{ grams}$, $U_o = 1.1 \text{ m/s}$. Fit parameters are: $k_c = 0.1 \text{ m/s}$ (both cases), and $D_{\text{ec}} = 1.67 \times 10^{-4} \text{ m}^2/\text{s}$ (0.55 mm test) and $3 \times 10^{-5} \text{ m}^2/\text{s}$ (2.58 mm test)).

Figure 4.13 Resistances to reaction for 0.55 mm diameter particle. ($T_{\text{bed}} = 1123 \text{ K}$, $m_{\text{LS}} = 30 \text{ grams}$, $U_o = 1.1 \text{ m/s}$. Fit parameters are: $k_c = 0.1 \text{ m/s}$, and $D_{cc} = 1.67 \times 10^{-4} \text{ m}^2/\text{s}$).

Figure 4.14 Resistances to reaction for 2.58 mm diameter particle. ($T_{bed} = 1123$ K, $m_{Ls} = 30$ grams, $U_o = 1.1$ m/s. Fit parameters are: $k_c = 0.1$ m/s, and $D_{ec} = 3 \times 10^{-5}$ m²/s).

Figure 4.15 Transient data changed into the form of Eqn. (2.76) for evaluation of τ_c

Figure 4.16 Log plot of calcination time constant vs. particle diameter ($U_o = 1.12$ m/s, $[CO_2]_i$ varies with temperature $[SO_2]_i = 1500$ ppm.. Tests run at $T = 1123$ K used 20 g batches and had no SO_2 injection. Lines shown are regression lines.)

Figure 4.17 Activation energy plot for calcination. (30 grams of Gilmore City formation limestone, $U_o = 1.12$ m/s, $[SO_2] = 1500$ ppm except as noted)

Figure 4.18 Extent of calcination at various temperatures for four particle sizes ($U_o = 1.12$ m/s, $m_{Ls} = 30$ g of Gilmore City formation limestone, $[SO_2]_i = 1480$ ppm.)

Figure 4.19 Calcination transients for two other limestones. ($T_{bed} = 1123$ K, $U_o = 1.1$ m/s, $m_{LS} = 20$ grams, $[SO_2]_i = 1480$ ppm.)

Figure 4.20 SEM photograph of unreacted limestone

Figure 4.21 SEM photograph of 2.58 mm limestone particle extracted after 2 minutes of reaction

Figure 4.22 Region A of particle in Fig. 4.21

Figure 4.23 Region B of particle in Fig. 4.21

Figure 4.24 Region C of particle in Fig. 4.21

Figure 4.25 Region D of particle in Fig. 4.21

Figure 4.26 Comparison of shrinking particle core model vs laboratory SO_2 transients ($U_o = 1$ m/s, $T_{\text{bed}} = 1123$ K, $m_{LS} = 20$ grams, $[\text{SO}_2]_i = 1510$ ppm)

Figure 4.27 Resistances to sulfation for 0.655 mm diameter particle. ($T_{bed} = 1123$ K, $m_{LS} = 20$ grams, $U_o = 1.1$ m/s. Fit parameters are: $k_s = 500$ m/s, $D_{es} = 1.7 \times 10^{-6}$ m/s, and $\tau_p = 760$ s. La Nauze correlation used for h_s).

Figure 4.28 Resistances to sulfation for 1.85 mm diameter particle. ($T_{\text{bed}} = 1123 \text{ K}$, $m_{\text{LS}} = 20 \text{ grams}$, $U_o = 1.1 \text{ m/s}$. Fit parameters are: $k_s = 500 \text{ m/s}$, $D_{\text{cs}} = 1.7 \times 10^{-6} \text{ m/s}$, and $\tau_p = 760 \text{ s}$. La Nauze correlation used for h_s).

Figure 4.29 Time constant chart to evaluate chemistry control. (30 grams Gilmore City formation limestone, $U_o = 1.1 \text{ m/s}$, $[SO_2]_I = 1500 \text{ ppm}$)

Figure 4.30 Initial concentration chart used to evaluate film mass transfer control. (30 grams Gilmore City formation limestone, $U_o = 1.1$ m/s, $[SO_2]_i = 1500$ ppm)

Figure 4.31 Time constant chart to evaluate pore diffusion control. (30 grams Gilmore City formation limestone, $U_o = 1.1 \text{ m/s}$, $[SO_2]_I = 1500 \text{ ppm}$)

Figure 4.32 Time constant chart to evaluate pore plugging control. (30 grams Gilmore City formation limestone, $U_o = 1.1 \text{ m/s}$, $[\text{SO}_2]_I = 1500 \text{ ppm}$)

Figure 4.33 Calcium utilization for a range of 16 different particle sizes

Figure 4.34 Plot of sulfation time constant versus particle diameter. (Gilmore City formation limestone, $U_o = 1.1$ m/s, τ_{sk} determined from Eqn. (2.127).)

Figure 4.35 Calcium utilization as a function of temperature for four particle sizes

Figure 4.36 Determination of activation energy for sulfation for four particle sizes. (Gilmore City formation limestone, $m_{LS} = 30 \text{ g}$, $U_0 = 1.1 \text{ m/s}$, τ_s determined from Eqn. (2.127).)

Figure 4.37 Calcium utilization as function of temperature for batch tests with lime and limestone.

Figure 4.38 Determination of activation energy for sulfation comparing batch additions of limestone vs. lime. Activation energies are: limestone, 4.03 kcal/mol; lime, 10.3 kcal/mol

Figure 4.39 Predicted CO₂ flux from various sized particles based on CO₂ transients.

Figure 4.40 Normalized SO_2 transients for lime and limestone.

Figure 4.41 Comparison of normalized SO₂ transient for washed and unwashed limestone batch additions.

Figure 4.42 Transient SO_2 response for varying concentrations of O_2

Figure 4.43 Comparison of normalized SO_2 transients for three limestones

a. Sulfation layer at $t = 2$ min.

b. Sulfation layer at $t = 8$ min.

c. Sulfation layer at $t = 16$ min.

d. Sulfation layer at $t = 40$ min.

e. Sulfation layer at $t = 80$ min.

Figure 4.44 SEM maps of sulfation at various times in the reaction.

Figure 4.45 Particle linescans at various stages of reaction

Figure 4.46 Comparison of transient gas analysis with SEM linescan analysis

Figure 4.47 t_v versus coal particle diameter

Figure 4.48 Comparison of 4x6 mesh batch tests of Illinois washed coal in bubbling fluidized bed and CFB boiler

Figure 4.49 τ_c vs. initial diameter for Illinois washed and Nova Scotia coals in CFB boiler

Figure 4.50 Burning rate per particle vs. initial diameter; Illinois washed coal tests in CFB boiler

Figure 4.51 CO₂ profile for batch test of 25.0 lb of 4x8 lignite in CFB boiler

Figure 4.52 Devolatilization time, t_v vs. initial diameter for Illinois washed coal, lignite, and Nova Scotia coal in CFB boiler

Figure 4.53 SO_2 emissions during limestone batch test ($T = 1120\text{--}1140\text{ K}$, $U_o \approx 4.5\text{ m/s}$, m_{Ls} 100 lb Gilmore City formation limestone, $d_p = 1.0\text{ mm}$)

Figure 4.54 Comparison of laboratory and power plant sulfation transients

Figure 4.55 Log-linear time constant chart comparing lab and full scale combustors

Figure 4.56 SEM component maps of power plant bottom ash showing sulfur rims (lower left map)

Figure 4.57 Bode plot of batch test of 5 g 14x16 mesh Kentucky coal in bubbling fluidized bed combustor

Figure 4.58 Devolatilization time t_v vs. initial diameter calculated using spectral analysis for batch tests in bubbling fluidized bed combustor

Figure 4.60 Bode plot of batch test of 5 g 6x7 coal in bubbling boiler

Figure 4.59 τ_c vs. initial diameter calculated using spectral analysis for batch tests in bubbling fluidized bed combustor

Fig. 4.61 Bode plot of batch test of 25 lb 14x16 mesh Illinois wash coal in CFB boiler