Abstract

MAO, DEMING. Particle Flow, Agglomeration, Mixing, Physical and Chemical Adsorption in Circulating Fluidized Bed Adsorbers (Under the direction of Dr. Jack R. Edwards and Dr. Andrey V. Kuznetsov)

Coal-utilization for energy production poses considerable environmental concerns as it results in emission of sulfur dioxide (SO₂), nitrogen oxide (NOₓ), fine particulate matter (PM), and trace heavy metals such as mercury vapor (Hg) during coal-combustion. Circulating Fluidized Bed Adsorbers (CFBAs) are regarded as a potentially effective technology to capture some of the above pollutants. In particular, one could use limestone to remove sulfur dioxide by chemical adsorption, and activated carbon to remove elemental mercury by physical adsorption. Also, sorbent particles could be used to capture fine PM or promote formation of clusters of larger PM.

In order to analyze CFBA systems in detail, a new approach has been developed for solving the Navier-Stokes equations for a gas-mixture/solids-mixture system. Submodels are also developed to be combined with the gas/solids hydrodynamics model to simulate capture of multiple pollutants. Specific tasks accomplished include the following.

1. A model for fine particle agglomeration in CFBAs has been developed. It can model the influence of different factors on agglomeration, such as the geometry of a CFBAs, the superficial gas velocity, initial particle size distribution (PSD), and type of agglomeration mechanism. It is found that the Brownian agglomeration mechanism can be neglected compared to agglomeration by mean shear and turbulence. Sorbent particles are shown to capture fine particles effectively for certain conditions. A simplified version of this model has been developed for coupling with the hydrodynamics model.
2. A mixing model based on a core-annulus model of a CFBA has been developed to simulate the particle residence time distribution (RTD). Thus, macrochemical reaction can be simulated by combining microchemical reaction dynamics with the particle RTD. This has been applied to simulate SO$_2$ removal by chemical adsorption onto dry lime.

3. A “gas mixture” and “solids mixture” model has been developed to simulate fine particle agglomeration onto sorbent particles, sulfur dioxide removal through chemical adsorption with lime, and mercury vapor removal through physical adsorption with activated carbon. The “gas mixture” is composed of fine PM, sulfur dioxide, mercury vapor, oxygen and inert gas; while “solids mixture” is composed of solids-1 and solids-2. Solids-1 is composed of lime (CaO) and CaSO$_4$, and solids-2 is activated carbon. These equations are similar to continuity equations appearing in the gas-solids hydrodynamics system and are integrated fully coupled with that system.

4. A new approach for solving the Navier-Stokes equations governing gas/solids two-phase flow with chemical reaction has been developed. The approach combines a time-derivative preconditioning strategy for a gas/solids two-phase flow model with extensions of low-diffusion flux-splitting upwinding techniques. The combined framework is used to simulate jet-induced bubble formation within a minimally fluidized bed, flow within a circulating fluidized bed without chemical reaction, a downward fluidized bed, and gas mixture/solids mixture flow within a prototype CFBA device. For bubble bed simulation, the model gives good results for bubble formation, growth and burst. For three-dimensional CFBAs, it can give good results compared with experimental data and can capture details of solids clustering phenomena. For downward fluidized bed, the model gives plausible results regarding the influence of superficial gas velocity on particle flow and mixing. Finally, simulations of a “bench-scale” CFBA reactor with combined SO$_2$, Hg and fine PM capture give reasonable
results for gas species and solids species, but further validation is needed.
Particle Flow, Agglomeration, Mixing, Physical and Chemical Adsorption in Circulating Fluidized Bed Adsorbers

by

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Biography

Deming Mao was born in Jiangsu, China. He got his B.Sc degree in Xi’An Petroleum Institute in 1992, where he became interested in fluid mechanics. He then went to Department of Mechanics in Zhejiang University for graduate study. After he got a M.S. degree in Fluid Mechanics in 1995, his interests were directed toward the application of fluid mechanics in engineering, especially in chemical engineering. He then worked in the Department of Chemical Engineering in Zhejiang University and the State Key Laboratory of Chemical Engineering Polymerization Branch to continue his interest in flow, mixing and chemical reaction. In 1999, he went to the Department of Chemical Engineering at University of Alberta to study meso-mixing in a continuous stirred tank reactor. From January of 2000, he has been doing research directed toward the development of novel techniques for simulating multi-phase flows and their applications to circulating fluidized bed adsorbers for multi-pollutant control.
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List of Symbols

Roman symbols:

\( a \)  
interfacial mass transfer area based on reactor volume

\( a_g \)  
gas sound speed

\( a_s \)  
solids sound speed

\( A \)  
cell area

\( A_1 \)  
limestone constant for \( SO_2 \) adsorption

\( A_{1-7} \)  
block matrix

\( A_{i,j,k}, B_{i,j,k}, C_{i,j,k} \)  
Jacobian matrix

\( B_1 \)  
limestone constant for \( SO_2 \) adsorption

\( C \)  
mass concentration of solid particle

\( C_1, C_2 \)  
constants in chemical reaction rate equations

\( C_{\text{eff}}^0, C_{\text{eff}}^1 \)  
activated carbon constants for mercury adsorption

\( C_D \)  
drag coefficient

\( C_S \)  
scaling constant for solids pressure

\( d_p \)  
particle diameter

\( E, F, G \)  
flux vectors in \( x, y, z \) directions

\( f \)  
wall friction factor

\( F_k \)  
k \(-th\) flux vectors in \( k \)-th directions under general coordinates

\( g \)  
gravity

\( G \)  
net solids flux (circulation rate)

\( h \)  
cell height

\( H \)  
riser height

\( k \)  
Boltzmann constant

\( K \)  
mass transfer coefficient based on interfacial area

\( M \)  
Jacobian matrix
$M_{CaO}$ molecular weight for $CaO$

$M_{CO_2}$ molecular weight for $CO_2$

$M_g, M_s$ Mach numbers for gas and solids

$M_{H_2O}$ molecular weight for $H_2O$

$M_{Hg}$ molecular weight for $Hg$

$M_{Inert}$ molecular weight for inert gas

$M_{N_2}$ molecular weight for $N_2$

$M_{ref,g}, M_{ref,s}$ reference Mach numbers for gas and solids

$M_{SO_2}$ molecular weight for $SO_2$

$n, n(\nu)$ particle size distribution function with volume the distributed variable

$N$ number of samples of sorbent particles size

$p_g$ gas pressure

$p_s$ solids pressure

$P$ pressure

$q$ flow rate based on fluctuation velocity

$q_1$ flux of solid particles outside of riser

$q_2$ flux of solid particles in the annulus region inside the riser

$q_3$ flux of fresh solid particles entering the CFBA

$Q$ flow rate based on mean velocity

$r_i$ $i$–th particle radius

$R$ general gas constant or residual column vector

$Re_s$ solids Reynolds number

$R_{Hg}$ physical adsorption rate for mercury

$R_{SO_2}$ chemical adsorption rate for sulfur dioxide

$s_{g,i}$ $i$–th gas source term

$s_{s,i}$ $i$–th solids source term
$S$  
source variable column vector or shear rate

t  
time

$T$  
temperature

$u_g, v_g, w_g$  
gas velocity components

$u_s, v_s, w_s$  
solids velocity components

$U$  
conservative variable column vector

$U_{mf}$  
minimum fluidization velocity

$U_{ref,g}, U_{ref,s}$  
reference velocities for gas and solids

$V$  
primitive variable column vector, or volume

$W$  
conservative variable column vector

$x, y, z$  
Cartesian coordinates

$X_{CaO}$  
$CaO$ mass fraction inside solids-1

$X_{gi}$  
i – th gas species mass fraction inside the mixture inert gas

$Y_{g1}$  
normalized concentration for fine particulate matter

$Y_{gi}$  
i – th gas species mass fraction inside mixture gas

$Y_{s1}$  
solids-1 mass fraction inside mixture solids

$Y_{s2}$  
solids-2 mass fraction inside mixture solids

**Greek symbols:**

$\alpha$  
volume fraction, or fresh particle ratio

$\beta$  
drag term or coagulation correlation

$\gamma$  
shear rate

$\epsilon_d$  
turbulent energy dissipation

$\varepsilon$  
voidage

$\varepsilon_{mf}$  
minimum fluidization voidage

$\eta$  
fine particle capture efficiency
θ scal parameter in LDFSS
κ fine particulate matter coagulation coefficient
λ eigenvalue
μ bulk viscosity
ν kinetics viscosity or fine particle volume
ρ density
τ pseudo time or residence time

Subscripts:
1/2 numerical cell interface
± positive/negative splittings
a annulus region
c core region
i, j i-th or j-th species

Supscripts:
± positive/negative splittings
c convection component
p pressure component
n physical time level
k pseudo time level
1 General Introduction

1.1 Introduction

According to forecasts on world fuel use, coal utilization in the next 60 years may increase by a factor of three or more [3]. For example, in China, about 75% total energy consumption comes from coal. This situation will continue for a long period in the future. In some districts of China, low-grade coal containing high ash and high sulphur, or even coal refuse has to be used because of the non-uniform distribution of energy resources and the shortage of energy supplies, leading to low combustion efficiency and high emission of harmful pollutants such as dust or fine particulate matter (PM), sulfur dioxide (SO$_2$), nitrogen oxide (NO$_x$), mercury vapor (Hg) and others. Statistical data shows that the major pollutants in the atmosphere come from the utilization of coal. For example, the Clean Air Act Amendments of 1990 listed 189 substances as hazardous air pollutants, and 37 of these substances have been detected in power plant emissions. The estimated percentages of atmospheric pollutants arising from coal-combustion is 87% for SO$_2$, 71% for CO, 67% for NO$_x$, 60% for fine PM, and 45% for mercury [4]. So the development of strategies that take advantage of coal utilization while controlling the emissions of harmful pollutants is very important.

The U.S. Environmental Protection Agency (EPA) is interested in developing novel emission-control technologies that can easily be retrofitted to existing coal-fired power plants. A partial area of emphasis is toward technologies that provide simultaneous control of multiple pollutants, such as fine PM, SO$_2$, and mercury vapor. One promising concept is the Circulating Fluidized Bed Adsorber (CFBA), which may utilize injection of different sorbents to remove multiple pollutants. For example, a CFBA could scrub SO$_2$ through adsorption onto calcinated limestone, and could eliminate mercury vapor through adsorption onto activated carbon. Increased
solids-gas contact and solids recycling promises both efficient pollutant removal and economy. A potential side benefit is the capture of fine particulate matter through agglomeration with sorbent particles.

In this work, we are developing modeling and simulation strategies for circulating fluidized bed adsorbers and other gas-solid reactors and hope to use these strategies in the design, analysis, and optimization of CFBA systems. Our activities combine CFD algorithms for simulating gas-solid hydrodynamics with sub-models representing the capturing or chemical conversion of particular pollutants through interaction with different sorbent types.

At present, three sub-models are considered: fine particulate matter adsorption onto sorbent particles, sulfur dioxide removal by interaction with calcinated limestone, mercury removal through interaction with activated carbon, and fine particle agglomeration due to collision between fine particles and sorbent particles. These sub-models are first formulated using 1-D reactor modeling concepts, then integrated into a computational fluid dynamics algorithm for simulating CFBA reactor hydrodynamics.

1.2 Outline of this work

An outline of this work is as follows. Section 2 describes sub-models for the different pollutant-removal processes considered in this work. Specifically, one-dimensional reactor-level models of fine PM agglomeration, $SO_2$ conversion and mercury conversion are described, as are simplified forms of these models suitable for embedding into the computational fluid dynamics code. Section 2 also presents the governing equations of two-phase gas-solids flow. A “mixture” formulation for the gas and solids phases is adopted, with different pollutant-capturing mechanisms described by source terms. Section 3 describes the numerical method utilized to solve the gas-
solid equations in three dimensions, while Section 4 provides some results to examine this method. Section 5 presents conclusions and provides directions for future work. Finally Jacobian matrices are listed in appendix A.
2 Model Development

2.1 A model for fine particle agglomeration in CFBAs

2.1.1 Introduction

CFBAs are becoming more widely used in industry for control of pollutant emissions from coal-fired power plants [5–7]. A potential side benefit of a CFBAs is the capture of fine particulate matter (PM) present in the flue gas. Increased solids-solids interactions may promote fine PM agglomeration, either with other fine PM or with sorbent, leading to larger particles that are more easily captured by filtration devices.

The objectives of this part of the work are to investigate the effects of geometry, flow conditions, sorbent particle distribution, and agglomeration mechanisms on fine particle agglomeration within prototypical CFBAs. The methodology combines a one dimensional hydrodynamics model for CFBA operation with the solution of the general dynamic equation of aerosol transport theory, considering only advection and agglomeration. The sections that follow briefly describe the hydrodynamics model and the aerosol transport model in detail. Selected results illustrating the effects of the variables mentioned above on a fine PM size distribution taken from recent experimental measurements from [8–10] are presented.

2.1.2 Core-annulus model

Before simulating fine particle agglomeration, the hydrodynamic behavior of a CFBAs must be modeled. This is done by using a core-annulus model presented by Berruti and Kalogerakis [11]. A schematic of the core-annulus model utilized for the solution of hydrodynamic problem in a CFBAs is shown in Fig 2.1; the core is a dilute suspension flowing upwards and the annulus is a denser film of particles moving downward in [11]. The model requires an experimental average voidage profile along the riser (or equivalently the pressure distribution), and the net solids circulation rate, $G$. It
can predict core voidage distribution, particle velocity distribution, and gas velocity distribution along the height of the riser.

![Diagram of a core-annulus model of the CFBA riser flow](image)

Figure 2.1: Core-annulus model of the CFBA riser flow

2.1.3 Particle agglomeration dynamics

The state of a spatially and chemically homogeneous particulate system is described by its size distribution density function, \( n_\nu(\nu, t) \), where \( n_\nu(\nu, t) \) is the number of particles per unit volume of fluid having volumes in the range from \( \nu \) to \( \nu + d\nu \). The dynamics of such a system, in which particles may collide and coagulate, are described by a general dynamics equation [12–19], written for one spatial dimension in Equation 2.1.

\[
\frac{\partial n}{\partial t} + \frac{\partial (nn_\nu)}{\partial z} = \frac{1}{2} \int_0^\nu \beta (\tilde{\nu}, \nu - \tilde{\nu}) n_\nu (\nu - \tilde{\nu}) d\tilde{\nu} \\
- \int_0^\infty \beta (\nu, \tilde{\nu}) n_\nu (\nu) d\tilde{\nu} \\
- \int_0^{\infty} \beta_s (\nu, \tilde{\nu}) n_s (\nu) n (\tilde{\nu}) d\tilde{\nu}
\]  

(2.1)

where \( n \) is the particle number density, \( n_s \) is the sorbent particle number density, and \( \beta \) is the collision frequency function. The initial and boundary conditions required
for Equation 2.1 in the CFBAs can be written as the following.

\[ n_\nu (z, 0) = 0 \quad (2.2) \]

\[ n_\nu (0, t) = n_0 \quad (2.3) \]

The first term on the right-hand side of Equation 2.1 represents the rate of accumulation of particles in the size range \((\nu, \nu + d\nu)\) by collision of two particles of volumes \(\nu - d\nu\) and \(d\nu\) to form a particle of volume \(\nu\) (assuming conservation of volume during coagulation). The second term represents the rate of loss of particles in the size range \((\nu, \nu + d\nu)\) by collision with all other finer particles. The third term represents the rate of loss of particles in the size range \((\nu, \nu + d\nu)\) by collision with all sorbent particles. Growth of sorbent particles due to fine particle agglomeration is neglected; the sorbent particles are assumed simply to act as a sink for fine particles.

To integrate the above equation numerically, a semi-implicit Euler method is used. Upwinding differencing is used for the spatial discretization and the accumulation term is treated explicitly. The discretization is as follows.

\[ \forall j \frac{n_{i,j}^{n+1} - n_{i,j}^{n}}{\Delta t} + \bar{u}_{g,j}A_{j-n_{i,j}^{n+1}} - \bar{u}_{g,j-1}A_{j-n_{i,j-1}^{n+1}} \]

\[ = \frac{1}{2} \forall j \sum_{l = i-k}^{i-1} \beta (\nu_k, \nu_l) n_{k,j}^{n} n_{l,j}^{n} \Delta \nu_k \]

\[ - \forall j n_{i,j}^{n+1} \sum_{m=1}^{\infty} \beta (\nu_i, \nu_m) n_{m,j}^{n+1} \Delta \nu_m \]

\[ - \forall j n_{i,j}^{n+1} \sum_{m=1}^{\infty} \beta_s (\nu_i, \nu_m) n_{s,j}^{n+1} \Delta \nu_s \]

In this section, four coagulation mechanisms, Brownian coagulation, mean shear coagulation, coagulation due to relative velocity between phases (also called kinematic coagulation), and turbulent coagulation, are considered [12].

For Brownian coagulation, the following correlation is utilized.

\[ \beta_b (r_k, r_i) = \frac{2KT}{3\mu} \left( \frac{1}{r_k} + \frac{1}{r_i} \right) (r_k + r_i) \quad (2.5) \]
For mean shear coagulation, the following correlation is utilized.

\[
\beta_s (r_k, r_i) = \frac{4}{3} (r_k + r_i)^3 \frac{d\bar{u}_g}{dr} \eta_{k,i} \tag{2.6}
\]

where \(\eta\) is the a capture efficiency to be defined later.

Kefa et al. [20] have found that gas velocity follows the power law as Equation 2.7 with the exponent \(n = 1/7\).

\[
u_g (r) = u_{g,\text{max}} \left(1 - \frac{r}{r_0}\right)^n \tag{2.7}
\]

With this profile, laminar shear is calculated by Equation 2.8.

\[
\frac{d\bar{u}_g}{dr} = \frac{\int_0^{r_0} du_g r dr}{\int_0^{r_0} r dr} = (n + 2) \frac{\bar{u}_g}{r_0} \tag{2.8}
\]

For turbulent coagulation, the following correlation is utilized.

\[
\beta_t (r_k, r_i) = \frac{4}{3} (r_k + r_i)^3 \left(\frac{\varepsilon_d}{\nu}\right)^{1/2} \tag{2.9}
\]

The influence of the average velocity difference, \(\Delta\bar{u}\), between sorbent and fine particles on agglomeration is accounted for by the following equation [21].

\[
\beta_r (r_k, r_i) = \pi (r_k + r_i)^2 \Delta\bar{u}\eta_{k,i} \tag{2.10}
\]

This mechanism only affects coagulation between fine particles and sorbent particles and thus contributes only to \(\beta_s\) in Equations 2.1 and 2.5.

The local velocity difference between sorbent and fine particles can be calculated by utilizing the terminal particle velocities, as:

\[
\Delta u = u_{ts} - u_{tf} \tag{2.11}
\]

Haider and Levenspiel [22] suggested the following empirical correlations for these
velocities.

\[ d_p^* = d_p \left[ \frac{\rho_f (\rho_s - \rho_g) g}{\mu^2} \right]^{1/3} \]  

(2.12)

\[ u_t^* = \left[ \frac{18}{(d_p^*)^2} + \frac{2.335 - 1.744 \phi_s}{(d_p^*)^{1/2}} \right]^{-1} \]  

(2.13)

\[ u_t = u_t^* \left[ \frac{\rho_g^2}{\mu (\rho_s - \rho_g) g} \right]^{-1/3} \]  

(2.14)

where \( \phi_s \) is the particle sphericity defined in Equation 2.15

\[ \phi_s = \left( \frac{\text{surface of sphere}}{\text{surface of a particle}} \right) \text{ same volume} \]  

(2.15)

In the annulus region, sorbent particles move downward, while fine particles move upward, so the average velocity difference between sorbent and fine particles can be calculated from the following equation.

\[ \Delta \bar{u} = \frac{\int_{r_c}^{r_0} (u_g + u_{ts}) r dr + u_{ts} \int_0^{r_c} r dr}{\int_0^{r_0} r dr} \]  

(2.16)

The capture efficiency for particle impaction due to viscous, shear-driven flow can be calculated from curve-fitting theoretical data provided in Fuchs [21].

\[ \eta_{k,i} = 1.289 \left[ \min (r_k, r_i) \right]^{1.948} \max (r_k, r_i) \]  

(2.17)

Capture efficiencies for Brownian and turbulence-driven coagulation are assumed to be unity. Correlations for parameters in the above equations can be found in [23] as follows.

\[ f_g = \frac{0.0791}{Re_g^{0.25}}, 2100 \leq Re_g \leq 100000 \]  

(2.18)

\[ \frac{1}{\sqrt{f_g}} = 2 \log \left( Re_g \sqrt{f_g} \right) - 0.8, Re_g \geq 100000 \]  

(2.19)

\[ Re_g = \frac{\bar{u}_g D}{\nu_g} \]  

(2.20)

\[ f_s = \frac{5.7 \times 10^{-2} \sqrt{gD}}{2 v_s} \]  

(2.21)

\[ \varepsilon_d = \frac{4}{D} \left[ \frac{f_g + f_s}{2} \right]^{3/2} \bar{u}_g^3 \]  

(2.22)
Although some alternative models [24,25] have been developed, the core-annulus model and the approach suggested by Kefa et al. [20] are utilized here because they make it possible to capture the main features of hydrodynamics and agglomeration in CFBA. This model suggests a simple but physically sound approach to obtaining the sorbent particle distribution as well as their velocity distribution. Sorbent particles are much larger (100 times larger in diameter) than fine particles; therefore, the growth of sorbent particles is currently ignored in this formulation. The results presented later illustrate the effects of including different coagulation mechanisms in the overall formulation; as a rule, Brownian, mean-shear and turbulence-driven mechanisms are assumed to affect coagulation between fine particles and other fine particles ($\beta$ in Equations 2.1 and 2.5) as well as coagulation between fine particles and sorbent particles ($\beta_s$ in Eqns. 2.1 and 2.5). Selected calculations illustrate the effects of including kinematic coagulation (Eqn.2.10) as part of $\beta_s$.

2.1.4 Initial fine particle and sorbent particle distributions

In the simulations, a lognormal distribution function for sorbent particles is assumed [26–28].

\[
\frac{n_s(\nu)}{n_{s_0}} = \frac{1}{3\sqrt{2\pi}ln\sigma} e^{-\frac{\nu^2(\nu)}{18n^2\sigma^2}}
\]

\[\nu_0 = \sqrt{\frac{1}{N} \sum_{i=1}^{N} n_s \nu_i^2}
\]

where $\nu$ and $\nu_0$ are the particle volume and geometric mean particle volume, respectively, and $\sigma$ is the geometric standard deviation of the size distribution. The sorbent particle number density distribution is calculated from the voidage distribution and the assumed lognormal shape distribution function. The total number of sorbent
particles $n_{s0}$ is determined by the mass balance.

$$1 - \varepsilon = \sum_{i=1}^{N} \frac{4}{3} \pi r_{si}^{3} n_{si}$$

(2.25)

where the average voidage $\varepsilon$ is obtained from the core-annulus model as a function of height within the riser section. For fine particles, a measured particle size distribution from Linak et al. [29, 30] is utilized. These authors used electrical mobility and light scattering methods to measure particulate matter generated from the burning of coal and oil in fire-tube boiler and refractory-lined combustors. This particle size distribution is shown in Fig.2.2, along with a log-normal one used in our earlier study [31].

Figure 2.2: Initial fine particle size distribution
2.1.5 Simulation results and discussion

Hydrodynamics of the CFBA s  Table 2.1 presents the sorbent and fine particle size information, and Table 2.2 presents typical operating parameters for the CFBA simulations, as taken from the work of Bader et al. [32]. Fig.2.3 shows the distributions of average voidage and core voidage in the CFBA. The average voidage distribution is calculated utilizing the axial density profile given in Bader et al. [32]. in their Fig. 2.2. The core voidage distribution is simulated by the model suggested in Berruti and Kalogerakis [11]. With the increase in riser height, the average voidage increases greatly and the core voidage increases less dramatically. This implies that the structure of the denser annulus region will change greatly according to the mass balance. When the superficial velocity is 9.5 m/s, the typical core-annulus structure appears and the radius of the core region remains almost constant above 3 m from the bottom of the CFBA. When the superficial gas velocity is 4.5 m/s, the characteristic S-shaped voidage distribution appears and high voidage occurs only at the top of the CFBA.

Table 2.1: Particle distribution parameters

<table>
<thead>
<tr>
<th>particle type</th>
<th>Sorbent particle</th>
<th>Fine particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average radius, ( \mu m )</td>
<td>76</td>
<td>2</td>
</tr>
<tr>
<td>Minimum radius, ( \mu m )</td>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>Maximum radius, ( \mu m )</td>
<td>1000</td>
<td>100</td>
</tr>
<tr>
<td>Geometric standard deviation, ( \sigma )</td>
<td>1.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Figure 2.4 shows the core radius distribution along the height of the CFBA. With the increase in the height, the core radius increases greatly for the lower gas superficial velocity of 4.5 m/s. This is in agreement with experimental results published by Bader et al. [32]. When the superficial gas velocity is raised to 9.5 m/s, the radius of the core region remains almost constant. Figure 2.5 presents the particle velocity in the
Table 2.2: Simulation parameters for coagulation in the CFBAs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbent particle diameter, (d_s)</td>
<td>76 (\mu)m</td>
</tr>
<tr>
<td>Fine particle diameter, (d_f)</td>
<td>0.01 (d_s)</td>
</tr>
<tr>
<td>CFBAs height</td>
<td>12.2 m</td>
</tr>
<tr>
<td>CFBAs diameter</td>
<td>0.305 m</td>
</tr>
<tr>
<td>Gas velocity</td>
<td>4.5 m/s, 9.5 m/s</td>
</tr>
<tr>
<td>Boltzman constant, (k)</td>
<td>1.381e-23 J/K</td>
</tr>
<tr>
<td>Gas temperature, (T)</td>
<td>293.15 K</td>
</tr>
<tr>
<td>Gas viscosity, (\mu)</td>
<td>(18.1 \times 10^{-6}) kg/ms</td>
</tr>
</tbody>
</table>

Figure 2.3: Predicted distribution of average and core voidage in Bader et al’s CFBA
Figure 2.4: Predicted distribution of core radius in Bader et al’s CFBA

Figure 2.5: Predicted particle average velocity in the core region in Bader et al’s CFBA
core region of a CFBA. The velocity decreases with the increase of height for the 4.5 m/s superficial gas velocity. It remains constant in the core region above 3 m from the bottom for the 9.5 m/s superficial gas velocity.

**Influence of collision mechanisms on agglomeration** Figure 2.6 shows the effect of different agglomeration mechanisms on fine particle distribution at the top of the CFBA for a gas superficial velocity of 4.5 m/s. Only Linak’s distribution is considered in this presentation; results from the lognormal distribution may be found in Ref [31]. When agglomeration is controlled by the Brownian mechanism only, the fine particle concentration changes insignificantly and some new large particles are generated. It is noted that the number of large particles decreases faster than that of fine particles for shear or turbulence agglomeration mechanisms. For example, some fine particles with a radius of $2.0 \times 10^{-6} m$ still exist at the top of the CFBA for shear agglomeration, but no fine particle of this radius exists at the top of the CFBA for turbulence agglomeration. When agglomeration is controlled by a combination of the above three mechanisms, no fine particles make it to the top of the CFBA; all of them are captured by sorbent particles.

When the superficial gas velocity is changed into 9.5 m/s, the number of new particles generated by collisions between fine particles is larger than for the superficial gas velocity of 4.5 m/s as shown in Figure 2.7. For example, the largest fine particle radius for 4.5 m/s is approximately $4.4 \times 10^{-6} m$, but the largest fine particle radius for 9.5 m/s is approximately $5.4 \times 10^{-6} m$. The number of new fine particles is approximately $10^6$ when the superficial gas velocity is 4.5 m/s, but is approximately $10^8$ when the superficial gas velocity is 9.5 m/s. This is because, at higher gas velocities, the number of sorbent particles in the CFBA is reduced, residence times are shorter, and fewer fine particles are captured by the sorbent. Except for the largest particles,
Figure 2.6: Fine particle size distribution at the top of the CFBA (4.5 m/s, Linak et al.’s PSD)
Figure 2.7: Fine particle size distribution at the top of the CFBA (9.5m/s, Linak et al’s PSD)
the general shape of the distribution is not affected by agglomeration, indicating that the Linak et al. [29,30] distribution has most probably reached a self-preserving state before entering the CFBA. This means that the terms in the General Dynamic Equation representing size-class loss or gain through collisions with other fine particles balance, and the initial distribution is simply advected along the riser section under the influence of the sink term representing capture by sorbent particles.

2.1.6 Summary

The key result for this presentation is that the PSD shape is somewhat independent of collision mechanism for Linak’s distribution, which is representation of that produced in actual coal-fired boilers. The dominant effect is that of a decrease in the total number of fine PM due to capture onto sorbent particles. Other results can be found in [31].
2.2 Particle flow, mixing, and chemical reaction in CFBAs

2.2.1 Introduction

A CFBA is a gas/solid contactor in which fine particles are transported vertically in a riser by a high velocity gas stream. After exiting the top of the riser, some of the solids are separated from the gas and recirculated to the base. When the solids are catalyst or chemical reactants, their activities will change with the reaction time, or residence time distribution (RTD). The RTD is produced by recirculating and mixing inside the circulating fluidized bed (CFB). The main hydrodynamics of the CFBs can be captured by the core-annulus flow structure model (Fig. 2.1).

Main features of this model are studied in detail in numerous publications [11, 23, 32]. The gas mixing in the CFB has been studied in detail in [33–39]. Compared with gas mixing, the particle residence time distribution and particle mixing are more important for the CFB because they affect chemical reaction rate and product distribution. Although there are quite a number of studies on particle mixing in the CFB [5, 8, 40–53], only a few models of particle mixing are published [41–43]. Due to the core-annulus structure, it is not suitable to use a one-dimensional dispersion equation to describe mixing in the CFB. On the basis of the core-annulus structure, the cell-mixing model is developed in the present work. In contrast with other published models [41–43], particle mixing in the present work is simulated directly without the utilization of any parameters (e.g., dispersion parameters) determined from regressing experimental data.

The dynamics of a chemical reaction for sulfur capture models can generally be divided into two groups [54]: lime models and reactor models. The lime models focus on explaining the lime (\(CaO\))-sulfur dioxide (\(SO_2\)) reaction using structural parameters of \(CaO\), such as pore and grain size, as input data [55–59]. These \(CaO\) models provide an important contribution to the understanding of the complex sulfation pro-
cess. The “reactor” models often attempt to explain the sulfur capture performance in fluidized bed boilers by combining models of gas and solid movement with relatively simple expressions of CaO reactivity. Unfortunately, most of the research has focused on the ideal chemical reaction dynamics for installations of a small size [54, 60]. The influence of scale-up is usually not considered. Some papers consider modeling of CFBs on the basis of the plug flow model [54], but they do not consider the influence of backmixing on reaction dynamics, and also do not consider the voidage distribution in the CFB. In reality, particles have different residence time distributions (RTDs) in the CFB, indicating differences between fresh and older particles. Chemical reaction rates for particles of different ages are different: fresh particles can yield a higher chemical reaction rate, while older particles generally have a lower reaction rate or do not participate in the reaction. Because the surface of older particles is covered by reacted material preventing reactants from contacting the inner core; less than half of CaO (outer layer of the particle) can be used to bond acid gases as shown in Fig.2.8 [54, 60].

In order to overcome some of the above shortcomings of existing simulation models, this section provides the method of combining flow, mixing, and reaction through a RTD as shown in Fig 2.9. Gas and particle concentration distributions can be simulated by computational fluid dynamics (CFD). In the present section, velocity distribution is obtained from a simple but efficient model, the core-annulus flow structure, and RTD is obtained by a mixing model suggested in this section. Thus, macrochemical reaction dynamics can be simulated based on microchemical reaction dynamics through coupling of RTD and concentration and velocity distributions in the CFB. The particles’ age distribution is obtained on the basis of RTD. Therefore, different chemical reaction rates are considered for particles of different ages. In order to use CaO most efficiently, most of the CaO leaving the CFBA from the
top is returned to the bottom of the CFB, as shown in Fig. 2.10. Thus, the design incorporates two circulation loops: one inside the riser section, which exists because of the upflow of particles in the core and downflow in the annulus section; and the other outside the riser, which exists due to recirculation of particles that exit the CFB. In Fig. 2.10, $\alpha$ stands for the ratio of the fresh particle flow rate, $q_3$, to the flow rate inside the riser, $G$, where $G$ is the sum of the fluxes of the fresh and recycled particles, $q_3$ and $q_1$, respectively.

![Active particle (young particle) Dead particle (old particle)](image)

Figure 2.8: Young particle’s and old particle’s structure

### 2.2.2 Particle mixing and reaction model

The following subsections present particle mixing and reaction models based on core-annulus model in section 2.1.2.

**Particle mixing model in the CFB** The main advantages of the core-annulus model are its simplicity and its high efficiency. It requires the input of only two measurable steady-state parameters: the experimental average voidage profile along the riser (or equivalently the pressure distribution along the CFBA height), and the
Figure 2.9: Microreaction, macroreaction dynamics and mass transfer

\[ q_3 = a \cdot G \]
\[ G = q_3 + q_1 \]

Figure 2.10: Particle motion inside the CFBA

CaO and SO₂ Conversion

Reaction Rate

RTD

CFD+Mixing

Vₜ, G, H, D, etc.

T, P, C, etc.
net solids circulation rate.

Figure 2.11: Mixing model

For the core-annulus structure shown in Fig. 2.1, the mixing cell can be meshed as shown in Fig. 2.11. Assuming ideal mixing within the cell, mixing behavior in the core region can be obtained from the mass balance.

\[
V_{c,j} \frac{dC_{c,j}}{dt} = Q_{c,j-1}C_{c,j-1} - Q_{c,j}C_{c,j} - Q_{r,j}C'_{c,j} + q_{c,j-1}C_{c,j-1} + q_{c,j}C_{c,j+1} + q_{r,j}C_{a,j} - q_{c,j-1}C_{c,j} - q_{c,j}C_{c,j} - q_{r,j}C_{c,j}
\]  

(2.26)

where \( V \) is the volume of the cell, \( Q \) is the flow rate based on mean velocity of solid particles, \( q \) is the fluctuation flow rate based on fluctuation velocity, \( C \) is the concentration of solid particles in the cell, and \( r \) stands for radial direction.
Figure 2.12: SO2 reaction in the core and annulus region

For the annulus region, mass balance can be presented as:

\[ V_{a;j} \frac{dC_{a;j}}{dt} = Q_{a,j-1}C_{c,j+1} - Q_{a,j-1}C_{a,j} + Q_{r;j}C_{c,j} \]

\[ + q_{a,j}C_{a,j+1} + q_{a,j-1}C_{a,j-1} + q_{r;j}C_{c,j} \]

\[ - q_{a,j}C_{a,j} - q_{a,j-1}C_{a,j} - q_{r;j}C_{a,j} \] (2.27)

In the present research, fine particles are assumed to be injected from the bottom of the CFBA riser. Equations 2.26 and 2.27 must be solved subject to the following initial condition that describes pulse injection of tracer particles. In the lower most cell \((j=1)\) of the core region, the concentration of tracer particles initially equals:

\[ C_{c,j} = C_0, \quad j = 1 \] (2.28)

In any other cell of the core region as well as in any cell of the annulus region, the concentration of tracer particles initially equals zero:

\[ C_{c,j} = 0, \quad j > 1 \]

\[ C_{a,j} = 0, \quad j \geq 1 \] (2.29)
These conditions are based on the assumptions that mixing in the cell can be regarded as ideal and three-dimensional effects can be neglected. The present cell mixing model can be extended to three dimensions if three-dimensional hydrodynamic information is furnished. Fluctuation velocity is assumed to be 15% of average mean velocity and constant in all regions. The number 15% is reasonable according to Lun [61], Mathiesen et al. [62], and Samuelsberg and Hjertager [63].

Chemical reaction model in the circulating fluidized beds Figures 2.12 and 2.13 illustrate mass conservation of \( \text{SO}_2 \) and \( \text{CaO} \), respectively. The mass transfer coefficient for \( \text{SO}_2 \) between the core and annulus regions is 0.25 according to Kruse et al. [35,36]. The model consists of Equations 2.30 to 2.38. Continuity equations in the core region are given below:

\[
\frac{\partial}{\partial t} (\rho_{\text{SO}_2} \alpha_g) + \frac{\partial}{\partial z} (\rho_{\text{SO}_2} \alpha_g v_g) = -R_{\text{SO}_2} \alpha_g - k a (\rho_{c,\text{SO}_2} - \rho_{a,\text{SO}_2}) \tag{2.30}
\]

\[
\frac{\partial}{\partial t} (\rho_{\text{CaO}} \alpha_{\text{CaO}}) + \frac{\partial}{\partial z} (\rho_{\text{CaO}} \alpha_{\text{CaO}} v_{\text{CaO}}) + \frac{\partial}{\partial r} (\rho_{\text{CaO}} \alpha_{\text{CaO}} u_{\text{CaO}}) = -R_{\text{CaO}} \alpha_{\text{CaO}} \tag{2.31}
\]

where \( k \) is the mass transfer coefficient based on interfacial area, \( a \) is the interfacial mass transfer area based on reactor volume, \( \rho_{c,\text{SO}_2} \) is the \( \text{SO}_2 \) density in the core region, \( \rho_{a,\text{SO}_2} \) is the \( \text{SO}_2 \) density in the annulus region, \( R_{\text{SO}_2} \) and \( R_{\text{CaO}} \) are chemical reaction rates for \( \text{SO}_2 \) and \( \text{CaO} \) respectively, and \( \alpha_g \) and \( \alpha_{\text{CaO}} \) are volume fractions for gas and \( \text{CaO} \), respectively.

For a one-dimensional formulation, Equation 2.31 can be recast as:

\[
\int \frac{\partial}{\partial t} (\rho_{\text{CaO}} \alpha_{\text{CaO}}) d\Omega + \int \frac{\partial}{\partial z} (\rho_{\text{CaO}} \alpha_{\text{CaO}} v_{\text{CaO}}) d\Omega + S = - \int R_{\text{CaO}} \alpha_{\text{CaO}} d\Omega \tag{2.32}
\]

where

\[
S = A [(\rho_{\text{CaO}} \alpha_{\text{CaO}} u_{\text{CaO}})|_{\text{annulus}} - (\rho_{\text{CaO}} \alpha_{\text{CaO}} u_{\text{CaO}})|_{\text{core}}] \tag{2.33}
\]

\[
A = 2\pi r_c h \tag{2.34}
\]
Figure 2.13: CaO reaction in the core and annulus region

where $\Omega$ is an element area in the core region or annulus region, $r_c$ is the radius of core region, and $h$ is the element height. The term with the derivative with respect to $r$ in Equation 2.31 can be interpreted as the mass exchange between the core region and the annulus region, thus the two-dimensional axially symmetrical equations can be simplified to one-dimensional equations based on the core-annulus structure by integrating over the core region or annulus region. These equations describe transport process in the axial direction only, and transport between the core and annulus regions is accounted for by the source term given by Equation 2.33.

In the annulus region, particle velocity is assumed to be equal to the terminal velocity of a single particle, $u_t$, and the voidage in the annular region is assumed to be that of a fluidized bed at minimum fluidization conditions [11, 53]. Since the annulus region is close to the wall, where gas velocity must satisfy a no-slip boundary condition, gas velocity in the annulus region must be very small and can be neglected.
Resulting continuity equations for the annulus region are:

\[
\frac{\partial}{\partial t} (\rho_{SO_2} \alpha_g) + 0 = -R_{SO_2} \alpha_g + ka (\rho_{c,SO_2} - \rho_{a,SO_2}) \quad (2.35)
\]

\[
\frac{\partial}{\partial t} (\rho_{CaO} \alpha_{CaO}) + \frac{\partial}{\partial z} (\rho_{CaO} \alpha_{CaO} v_{CaO}) + \frac{\partial}{\partial r} (\rho_{CaO} \alpha_{CaO} u_{CaO}) = -R_{CaO} \alpha_{CaO} \quad (2.36)
\]

The microchemical reaction rate is studied in detail in Abanades et al. [64], Mattisson and Lyngfelt [54,60] and Qiu et al. [65]. In the present research, the chemical reaction rate is taken from Mattisson and Lyngfelt [54] because they considered the influence of particle age on the reaction rate. In the simulations, the $CaO$ is assumed to be completely calcinated, consisting of 100% $CaO$. The influence of $CaO$ integrity and its particle structure are reflected through the constants $C_1$ and $C_2$. The chemical reaction rates are then given by Equations 2.37 and 2.38.

\[
R_{CaO} = C_{CaO_0} \frac{C_1 p_{SO_2}}{C_1 C_2 p_{SO_2} \tau + 1} \int_0^\infty \frac{c_1^{\frac{p_{SO_2 i} + p_{SO_2 i-1}}{2}}}{c_1^{\frac{p_{SO_2 i-1}}{2}}} dc
\]

\[
R_{SO_2} = \rho \alpha (1 - \alpha_g) \frac{M_{SO_2}}{M_{CaO} C_{CaO_0}} R_{CaO} \quad (2.37)
\]

where $i$ is the cell number, $\tau$ is the residence time, $\rho$ is the $CaO$ density, $\alpha$ is the ratio of fresh particles entering the bottom of CFBA to all particles, and $p_{SO_2 i}$ is the $SO_2$ pressure in the $i$th element. The pressure of $SO_2$ can be calculated from its density by utilizing the ideal gas equation of state.

\[R_{SO_2} = \rho \alpha (1 - \alpha_g) \frac{M_{SO_2}}{M_{CaO} C_{CaO_0}} R_{CaO} \quad (2.38)\]

2.2.3 Simulation results and discussions

Table 2.3 presents values of operating parameters used in the CFBA simulations. These values are taken from the work of Bader et al. [32].

RTD distribution in the CFBA Figure 2.14 presents particle RTD at the bottom of the CFBA when the superficial gas velocity is 4.5 m/s. Residence time increases
Table 2.3: Simulation parameters in the CFBAs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle average diameter</td>
<td>76 $\mu$m</td>
</tr>
<tr>
<td>Lime density</td>
<td>2620 kg/m$^3$</td>
</tr>
<tr>
<td>CFBAs height</td>
<td>12.2 m</td>
</tr>
<tr>
<td>CFBAs diameter</td>
<td>0.305 m</td>
</tr>
<tr>
<td>Gas velocity</td>
<td>4.5 m/s, 9.5 m/s</td>
</tr>
<tr>
<td>$SO_2$ partial pressure at the entrance</td>
<td>15 kPa, 150 kPa</td>
</tr>
<tr>
<td>Gas temperature</td>
<td>193.15 k</td>
</tr>
<tr>
<td>Gas viscosity</td>
<td>$18.1 \times 10^{-6}$ kg/ms</td>
</tr>
</tbody>
</table>

Figure 2.14: RTD distribution in the core region at the bottom, 4.5 m/s
with the decrease of the portion of fresh particles among the injected particles, reflected by the ratio of fresh particles, $\alpha$. For example, when $\alpha$ decreases from 0.1 to 0.01 and 0.001, the residence time at a relative concentration of $10^{-9}$ increases from 450 s to 4,500 s and 450,000 s, respectively. At the same time, there is an oscillation phenomenon during the first 50 seconds. This is due to the circulation loops that exist inside and outside the riser section. In the outer circulation loop, $(1 - \alpha)$ of all particles return from the top of CFBA to the bottom. Both circulation loops produce concentration oscillation in the CFBA.

$SO_2$ and $CaO$ distribution in the CFBA, 4.5 m/s case Figure 2.15 shows the partial pressure of $SO_2$ at the top of CFBA versus reaction time. The simulation is unsteady (initial $SO_2$ partial pressure is 15 kPa, and initial $CaO$ concentration is zero). With the increase of the fraction of fresh $CaO$, $\alpha$, the partial pressure of $SO_2$ decreases with time until it comes to a steady state; after that, the amount of reacted $CaO$ and partial pressure of $SO_2$ does not change. For example, partial pressure of $SO_2$ attains 11.4 kPa after approximately 150,000 seconds. It takes a shorter time to come to a steady state when $\alpha$ is larger. For example, the time required to attain a steady state decreases from 150,000 to 5,000 seconds when $\alpha$ increases from $10^{-4}$ to $9 \times 10^{-4}$.

Figure 2.16 shows the steady state distribution of the $SO_2$ partial pressure in the core region of the CFBA when the velocity is 4.5 m/s. $SO_2$ partial pressure decreases with the increase of the distance from the bottom, which is due to the chemical reaction. At the same time, the reaction rate of $SO_2$ decreases from the bottom to the top, which can be seen from the decrease of $SO_2$ partial pressure from the bottom to the top. At the bottom, the percentage of fresh particles is the largest. As the reaction proceeds, the concentration of fresh particles decreases as particles become older.
Figure 2.15: SO2 concentration at the exit of CFBA
Figure 2.16: SO₂ partial pressure in the core region, 4.5 m/s
while they move higher in the CFBA. Therefore, the \( \text{CaO} \)'s activity will decrease and the reaction rate will decrease with the increase of the distance from the bottom as well. When the fresh-to-old particles ratio, \( \alpha \), increases, the \( \text{SO}_2 \) partial pressure decreases because more fresh particles that have higher chemical reaction rate come into the riser section. For example, \( \text{SO}_2 \) partial pressure at the outlet is 11.4 kPa for \( \alpha = 10^{-4} \) and almost zero for \( \alpha = 9 \times 10^{-4} \).

Figure 2.17: Influence of ratio, \( \alpha \), on \( \text{SO}_2 \) at the exit of the CFBA

Influence of ratio \( \alpha \), on \( \text{SO}_2 \) and \( \text{CaO} \) distributions  To find the quantity of \( \text{CaO} \) that is required for specified removal of \( \text{SO}_2 \), the ratio \( \alpha \) must be determined. Figure 2.17 shows influence of the ratio \( \alpha \) on the partial pressure of \( \text{SO}_2 \) at the exit of
Figure 2.18: Influence of ratio, $\alpha$, on $CaO$ at the exit of the CFBA
CFBA for different superficial gas velocities and different inlet SO$_2$ partial pressures. For the same inlet SO$_2$ partial pressure, less CaO or a smaller ratio $\alpha$ is required to remove SO$_2$ completely for a lower superficial gas velocity. To remove more SO$_2$, a larger amount of CaO or a larger ratio $\alpha$ is needed. This is because the number of particles in the core region for low superficial gas velocity is larger than that for the high superficial gas velocity.

Figure 2.18 shows corresponding CaO concentration distributions at the exit of the CFBA. SO$_2$ removal increases with the increase of the ratio $\alpha$. Alternatively, higher original SO$_2$ partial pressure at the entrance of the CFBA requires more CaO. For example, CaO concentrations of 1,210 and 1,235 kg/m$^3$ are required for partial pressures of 15 and 150 kPa, respectively.

### 2.2.4 Summary

A method of combining flow, mixing, and chemical reaction for CFBA has been developed, and a mixing model based on flow field to calculate RTD has been developed as well. The method and these models can successfully simulate RTD distribution, SO$_2$ distribution, CaO concentration distribution. They can predict the amount of CaO needed for different superficial gas velocities and different partial pressures at the inlet to the CFBA. The detailed results can be found in our work [66].

The key result is that reaction time from beginning to steady state is of the order of hours. It is very difficult to simulate such long-duration processes using computational fluid dynamics, and the use of a RTD allows a more economical analysis.
2.3 Mercury adsorption model by activated carbon in CF-BAs

2.3.1 Introduction

Most of the mercury in water, soil, sediments, or biota (i.e., all environmental media except the atmosphere) is in the form of inorganic mercury salts and organic forms of mercury (methylmercury). According to health studies, exposure via ingestion of methylmercury poses the most serious health risk, dietary methymercury is almost completely absorbed into the blood and distributed to all issues including the brain; it also readily passes through the placenta to the fetus and fetal brain. Exposure to elemental and inorganic mercury forms via inhalation and ingestion can present serious health risks if doses are acute; however, most health effects as a result of exposure are of a longer-term, leading to dysfunctional organs/systems as studied by Olson et al. [67].

According to the “Mercury Study Report to Congress” [4], 45.7% of mercury emissions generated are from coal-combustion processes. So the development of methods for controlling mercury emissions is very important. Many research efforts [67–72] have shown that activated carbon can be an effective sorbent for capturing elemental mercury. Recent results show that mercury adsorption capacity of activated carbon is dependent on temperature, mercury species, mercury concentration, other flue gas constituents, and the structure of the activated carbon itself, particularly pore structure (mesopores, 1-25 \( nm \), micropores, 0.4-1.0 \( nm \), and sub-micropores <0.4 \( nm \)).

Most of the work due to date has utilized a fixed-bed system [67,68,70,73], where the flue gas is passed through a stationary bed of activated carbon. Thus, there are some difficulties in extending these results to fluidized bed systems. Other studies have assumed simplified flow such as plug flow in a riser or tube [71,74,75], but did not consider the particle mixing effects that occur in real reactor geometries. All of
these are for activated carbon injection into a straight duct; not a circulating loop.

Activated carbon has a long age of reactivity, usually of the order of hours [67, 70, 73], but the adsorption activity can decrease greatly as the exposure time increases. On the other hand, the average residence time of flue gas in a CFBA is very short, of the order of seconds. Thus, plenty of activated carbon should be recirculated for both economics and efficiency. During the circulation-loop, activated carbon particle mixing occurs between newly-injected fresh particles and older circulating particles. How to get a reasonable average adsorption rate for mercury capture by activated carbon is very important for developing models for mercury removal within a CFBA.

2.3.2 Mercury vapor adsorption model in general transport equation

In this work, we simulate only the recycle of fresh particles over times characteristic of the residence time of the flue-gas within the CFBA. Over this period, the catalyst activity can be regarded as a constant given by the initial rate of mercury uptake [68].

Vidic et al. [68] measured vapor-phase mercury removal by activated carbon within a fixed-bed reactor. They measured the initial rate of mercury uptake, $r_0$, as a function of the initial mercury concentration, $C_0$, for three kinds of activated carbon: a virgin bituminous coal-based activated carbon (BPL), a commercially available sulfur impregnated activated carbon (HGR), and a BPL carbon impregnated with sulfur (BPL-S).

$$r_0 = \left( \frac{dC}{dt} \right)_{t=0}$$

(2.39)

where $r_0$ is the initial rate of mercury uptake per unit mass of activated carbon (mmol Hg/sec · mg), and $C_0$ is the initial vapor-phase mercury concentration (mmol Hg/L). Their results may be summarized by the following curve fits at gas temperature of 140°C.

$$BPL : \quad -r_0 = 1.09 \cdot 10^{-6} \times C_0^{0.67}$$
$$BPL - S : \quad -r_0 = 1.12 \cdot 10^{-4} \times C_0^{0.72}$$
$$HGR : \quad -r_0 = 1.66 \cdot 10^{-4} \times C_0^{0.80}$$

(2.40)
For the mercury concentration of 110 μg/m³, an increase in gas temperature showed little impact on the rate of mercury uptake and on the adsorption equilibrium. On the other hand, for the higher initial vapor-phase mercury concentrations, higher temperatures resulted in lower overall mercury uptake, which is characteristic of a exothermal adsorption process. The concentration range tested in the experiment for initial mercury is between 110 μg/m³ and 1,080 μg/m³. As shown later, the uptake rates given above can be reformulated as a source term for a mercury vapor transport equation.

2.4 A “gas mixture” and “solids mixture” model for two-phase flow, agglomeration, and adsorption in CFBAs

There are many models for two-phase gas-solids flow, with two types, the discrete approach and the continuum approach, most often used. In the discrete approach, only the gas (or continuum) phase is modeled through the Navier-Stokes equations. The motion of solid particles is treated by a Lagrangian approach, and particles are assumed to interact with each other through binary, instantaneous, inelastic or elastic collisions as well as being influenced by the gas phase through drag correlations and other mechanisms. Each particle thus has an equation to describe its evolution, and the form of the collision model is very important. This method can simulate the formation of solids clusters with little or no numerical dissipation, but it is limited by the particle number. Even with the increase of the computer capacity, only a “small” number of particles can be simulated, for example, Helland et al. [76] simulated 250,000 particles inside a fluidized bed. The occupied solids volume was just 2.09 × 10⁻⁶ m³ or 2.09 cm³, which is much smaller than that achieved in industry-scale gas-solids reactors. The simulated example listed later would have required 1.11 × 10¹⁰ particles in the CFBA for an average volume fraction of 3% solids, if a discrete particle-tracking approach were used.
The continuum approach regards both the gas and solids phases as interpenetrating continuum media. There are actually four main kinds of models: the homogeneous model, the mixture model, the drift flux model, and the separated-phase model. The homogeneous model treats the mixture as a pseudo-fluid, which obeys all the laws of single-phase flow. The mixture model also assumes that both phases have the same velocity, pressure and temperature; it can, however, provide non-equilibrium volume fraction information by solving a separate continuity equation for one of the phases. The drift model is similar to the mixture model, but it can consider the velocity difference between the two phases. The velocity difference is modeled by a constitutive equation, which is usually valid for small velocity differences or small Stokes relaxation times between the two phases. The separated-phase models describe the motion of each phase with separate continuity, momentum and energy equations. Coupling between the phases is through source terms representing mass, momentum, and energy exchange mechanisms. The separated-phase models [24, 77–86], are generally considered more realistic but are more expensive to solve numerically.

Gas-solid flows are normally found in a chaotic state, but one with some evidence of organized structure. Some of this chaotic behavior may be due to fluid turbulence [87–89]; some may due to collision dynamics [90,91]; and some may due to interactions between particles and gas at the so-called “meso-structure” level [1, 2, 92]. Kinetic theories of granular flows [24,93,94] have been proposed to account for some of these processes. Such closures model the effective solids viscosity, solids pressure, and particle phase stresses in terms of a granular temperature characteristics of small-scale interactions.

As pointed by Zhang and VanderHeyden [85] and Liu [95], kinetic theory of granular flows accounts for the effects of direct particle-particle collisions. Strictly speaking, these kinetic theories are most appropriate in granular systems where par-
particle inertia is dominant compared with interstitial fluid effects. However, for fluidized beds, the interstitial fluid plays an important role and can substantially affect particle-particle interactions. In these cases, the direct application of kinetic theories is conceptually questionable. As kinetic theory potentially accounts for nonlinear interactions occurring at small scales, one may wonder where simplified models may suffice for calculations on well-resolved, three-dimensional domains, where small-scale interactions can be captured directly.

One purpose of the present work is to attempt to better understand the basic behavior of the simple gas-solid flow equations before introducing any complicated granular-temperature or two-phase turbulence models. We use high resolution scheme and fine grids to solve these equations, and as such, we hope to progress toward a “large-eddy-simulation” level of modeling of fluidized bed reactor physics, in which macro-scale dynamical features such as solids clusters are captured rather than modeled. The developments outlined herein are based on Gidaspow’s hydrodynamics model B [23], a gas-solid model that is rendered hyperbolic in time by concentrating gas pressure effects solely within the gas phase and solids pressure effects within the solids phase. The governing equations are written below in Cartesian coordinates.

\[
\frac{\partial U}{\partial t} + \frac{\partial (E - E_v)}{\partial x} + \frac{\partial (F - F_v)}{\partial y} + \frac{\partial (G - G_v)}{\partial z} = S, \tag{2.41}
\]
where

\[
\begin{bmatrix}
\rho_g \alpha_g Y_{g1} \\
\rho_g \alpha_g Y_{g2} \\
\rho_g \alpha_g Y_{g3} \\
\rho_g \alpha_g Y_{g4} \\
\rho_g \alpha_g u_g \\
\rho_g \alpha_g v_g \\
\rho_g \alpha_g w_g \\
\rho_s \alpha_s Y_{s,1} X_{CaO} \\
\rho_s \alpha_s Y_{s,1} \\
\rho_s \alpha_s \\
\rho_s \alpha_s u_s \\
\rho_s \alpha_s v_s \\
\rho_s \alpha_s w_s
\end{bmatrix}
= \begin{bmatrix}
\rho_g \alpha_g u_g Y_{g1} \\
\rho_g \alpha_g u_g Y_{g2} \\
\rho_g \alpha_g u_g Y_{g3} \\
\rho_g \alpha_g u_g Y_{g4} \\
\rho_g \alpha_g u_g u_g + p_g \\
\rho_g \alpha_g u_g v_g \\
\rho_g \alpha_g u_g w_g \\
\rho_s \alpha_s u_s Y_{s,1} X_{CaO} \\
\rho_s \alpha_s u_s Y_{s,1} \\
\rho_s \alpha_s u_s \\
\rho_s \alpha_s u_s u_s + p_s \\
\rho_s \alpha_s u_s v_s \\
\rho_s \alpha_s u_s w_s
\end{bmatrix}
= \begin{bmatrix}
\rho_g \alpha_g v_g Y_{g1} \\
\rho_g \alpha_g v_g Y_{g2} \\
\rho_g \alpha_g v_g Y_{g3} \\
\rho_g \alpha_g v_g Y_{g4} \\
\rho_g \alpha_g v_g u_g \\
\rho_g \alpha_g v_g v_g \\
\rho_g \alpha_g v_g w_g \\
\rho_s \alpha_s v_s Y_{s,1} X_{CaO} \\
\rho_s \alpha_s v_s Y_{s,1} \\
\rho_s \alpha_s v_s \\
\rho_s \alpha_s v_s u_s \\
\rho_s \alpha_s v_s v_s + p_s \\
\rho_s \alpha_s v_s w_s
\end{bmatrix}
\]

\[
G = \begin{bmatrix}
\rho_g \alpha_g w_g Y_{g1} \\
\rho_g \alpha_g w_g Y_{g2} \\
\rho_g \alpha_g w_g Y_{g3} \\
\rho_g \alpha_g w_g Y_{g4} \\
\rho_g \alpha_g w_g u_g \\
\rho_g \alpha_g w_g v_g \\
\rho_g \alpha_g w_g w_g + p_g \\
\rho_s \alpha_s w_s Y_{s,1} X_{CaO} \\
\rho_s \alpha_s w_s Y_{s,1} \\
\rho_s \alpha_s w_s \\
\rho_s \alpha_s w_s u_s \\
\rho_s \alpha_s w_s v_s \\
\rho_s \alpha_s w_s w_s + p_s
\end{bmatrix}
= \begin{bmatrix}
s_{g1} \\
s_{g2} \\
s_{g3} \\
s_{g4} \\
s_g \\
\beta (u_s - u_g) + s_{mtm,g,x} \\
\beta (v_s - u_g) + s_{mtm,g,y} \\
\beta (w_s - w_g) + s_{mtm,g,z} - \rho_g g \\
s_{s,1} \\
s_{s,1} \\
s_s \\
\beta (u_g - u_s) + s_{mtm,s,x} \\
\beta (v_g - v_s) + s_{mtm,s,y} \\
\beta (w_g - w_s) + s_{mtm,s,z} - (\rho_s - \rho_g) \alpha_s g
\end{bmatrix}
\]

(2.43)
In these, $Y_{g1}$ is the normalized fine particle number density; $Y_{g2}$ is the mass fraction of sulfur dioxide; $Y_{g3}$ is the mass fraction of mercury vapor; $Y_{g4}$ is the mass fraction of oxygen; $X_{CaO}$ is the mass fraction of $CaO$ referenced to the mass of the first solids phase (solids-1) with components of $CaO$ and $CaSO_4$; $Y_{s1}$ is the mass fraction of solids-1 referenced to the total solids mass; $Y_{s2} = 1 - Y_{s1}$ is the mass fraction of activated carbon (solids-2) referenced to the total solids mass; $\rho_g$ is the mixture gas density; and $\rho_s$ is the mixture solids density. All of these are defined in Equation 2.52. $p_g$ and $p_s$ are gas and solids pressure, respectively; $\alpha_g$ and $\alpha_s$ are gas voidage and solids voidage, respectively; $u_g$, $v_g$ and $w_g$ are gas velocities in the $x$, $y$ and $z$ direction, respectively; $u_s$, $v_s$ and $w_s$ are solids velocities in $x$, $y$ and $z$ direction, respectively; $g$ is gravity, $\beta$ is the drag term, $s_{g1}$ is the source term for fine particle matter, $s_{g2}$ to $s_{g4}$ are the source terms for sulfur dioxide, mercury and oxygen, respectively, $s_g$ is the source term for the gas mixture, $s_{s1}$ is the source term for $CaO$, $s_{s1}$ is the source term for solids-1, and $s_s$ is the source term for the solids mixture continuity equation.
Gas-solids drag coefficients for different solids concentration are as follows [23].

\[ \beta = 150 \left( \frac{\alpha_s}{\alpha_g} \right)^2 \frac{\mu}{d_p^2} + 1.75 \rho_g \left( \frac{\alpha_s}{\alpha_g} \right) \frac{V_g - V_s}{d_p}, \quad \alpha_g \leq 0.8 \]

\[ \beta = 0.75C_D \frac{\alpha_s \rho_g |V_g - V_s| \alpha_g^{-2.65}}{d_p}, \quad \alpha_g > 0.8 \]  

(2.45)

In the preceding expressions, \( \mu \) is the gas viscosity (assumed constant), \( d_p \) is the particle diameter, and \( C_D \) is the drag coefficient.

\[ C_D = \frac{24}{Re_s} (1 + 0.15 Re_s^{0.687}), \quad Re_s < 1,000 \]

\[ Re_s = 0.44, \quad Re_s \geq 1,000 \]  

(2.46)

The form for the solids pressure is taken from Boivin et al. [96].

\[ p_s = \rho_s C_s \left[ \alpha_s + 2\alpha_s,\text{max} \ln(1 - \frac{\alpha_s}{\alpha_s,\text{max}}) - \frac{\alpha_s \alpha_s,\text{max}}{\alpha_s - \alpha_s,\text{max}} \right] \]  

(2.47)

where \( \alpha_s,\text{max} \) is the solids void fraction at maximum compaction (taken as 0.64) and \( C_s \) is a scaling constant (taken as 0.02 for most calculations). A solids "sound speed" can be defined through the relation

\[ \rho_s \alpha_s^2 = \frac{\partial p_s}{\partial \alpha_s} = \rho_s C_s \left( \frac{\alpha_s}{\alpha_s - \alpha_s,\text{max}} \right)^2 \]  

(2.48)

The constitutive relation between stress and strain rate for a Newtonian compressible gas or solids is

\[ \tau_{ij,k} = \alpha_k \left[ \mu_k \left( \frac{\partial u_{k,i}}{\partial x_{k,j}} + \frac{\partial u_{k,j}}{\partial x_{k,i}} \right) - \frac{2}{3} \mu_k \frac{\partial u_{k,m}}{\partial x_{k,m}} \delta_{ij} \right] \]  

(2.49)

where \( k \) is gas or solids. Solids viscosity is zero in the present work. The molecular diffusion velocity of the \( i^{\text{th}} \) component in gas phase in the \( j^{\text{th}} \) direction, \( u_{i,j}^d \), is expressed using Fick’s law:

\[ u_{i,j}^d = -\frac{D}{Y_{g,i}} \frac{\partial Y_{g,i}}{\partial x_j} \]  

(2.50)
where $D$ is the diffusion coefficient. Fick’s law can also be rewritten using the mixture density $\rho_g$, the gas mixture viscosity $\mu_g$, and the gas phase volume fraction by way of the Schmidt number, $Sc = \frac{\mu_g \alpha_g}{\rho_g \alpha_g D}$, and a constant Schmidt number is assumed ($0.72$).

$$\rho_g Y_{g,i} \alpha_g u_{i,j}^q = -\frac{\mu_g \alpha_g}{Sc} \frac{\partial Y_{g,i}}{\partial x_j}$$

(2.51)

Some of the above variables are defined below.

$$Y_{gi} = \frac{\rho_{g,i}}{\sum i=2 \rho_{g,i}}$$

$$\rho_g = \sum_{i=2}^N \rho_{g,i} = \frac{\rho_{g}}{RT} \left( \frac{y_{g2}}{M_{SO2}} + \frac{y_{g3}}{M_{Hg}} + \frac{y_{g4}}{M_{O2}} + \frac{1-y_{g2}-y_{g3}-y_{g4}}{M_{inert}} \right)$$

$$\frac{1}{\rho_s} = \frac{Y_{s,1}}{\rho_{s,1}} + \frac{1-Y_{s,1}}{\rho_{s,2}}$$

$$\frac{1}{\rho_{s,1}} = \frac{X_{CaO}}{\rho_{CaO}} + \frac{1-X_{CaO}}{\rho_{CaSO4}}$$

$$\frac{1}{M_{inert}} = \frac{X_{g,1}}{M_{N2}} + \frac{X_{g,2}}{M_{CO2}} + \frac{X_{g,3}}{M_{H2O}}$$

(2.52)

$$\alpha_g + \alpha_s = 1$$

$$Y_{s1} = \frac{\rho_{s1} \alpha_{s1}}{\rho_{s1} \alpha_{s1} + \rho_{s2} \alpha_{s2}}$$

$$Y_{s2} = \frac{\rho_{s2} \alpha_{s2}}{\rho_{s1} \alpha_{s1} + \rho_{s2} \alpha_{s2}}$$

$$\alpha_{s1} = \frac{Y_{s1} \rho_{s1} \alpha_{s1} + \rho_{s2} \alpha_{s2}}{\rho_{s1}} = Y_{s1} \frac{\rho_{s1} \alpha_{s1}}{\rho_{s1}}$$

$$\alpha_{s2} = \frac{Y_{s2} \rho_{s1} \alpha_{s1} + \rho_{s2} \alpha_{s2}}{\rho_{s2}} = Y_{s2} \frac{\rho_{s2} \alpha_{s2}}{\rho_{s2}}$$

In this, $N$ is the number of gas species including the normalized number density of fine PM, $M_{SO2}$, $M_{Hg}$, $M_{O2}$, $M_{N2}$, $M_{CO2}$, $M_{H2O}$, and $M_{inert}$ are molecular weights for $SO_2$, $Hg$, $O_2$, $N_2$, $CO_2$, $H_2O$, and inert gas, respectively; $\rho_s$ is the density for solids-2 (activated carbon), $X_{g,1}$, $X_{g,2}$, and $X_{g,3}$ are fixed mass fractions of $N_2$, $CO_2$ and $H_2O$ inside the inert gas, respectively.
2.5 Sub-model development for general forms
2.5.1 Fine particulate matter agglomeration

According to the previous chapter and our research [31], the shape of fine particle size distribution does not change significantly with agglomeration if the distribution is self-preserving, such as that of Linak et al. [29,30]. So the first term and second term on the right hand of Equation 2.1 can be ignored. These terms represent collisions between fine PM and other fine PM. The term left on the right hand side represents fine particle agglomeration onto sorbent particles, and it acts as a sink for fine PM number density. Assuming that the shapes of the sorbent and fine PM distributions do not change, we can simplify the source term as in equation 2.53

\[ s_{g,1} = -\kappa_s \alpha_s \rho_g \alpha_g Y_{g,1} \]  

(2.53)

where \( Y_{g,1} \) is the normalized fine particle number density function, and \( \kappa_s \) is a function of the particle collision method and particle size distribution.

\[ \kappa_s = \frac{\int_{\nu_d}^{\nu_s} [\int_{\nu_d}^{\infty} \beta (\nu_s, \nu) f_s (\nu_s) f (\nu) d\nu_s] d\nu}{\int_{\nu_d}^{\nu_s} \nu_s f_s (\nu_s) d\nu_s} \]  

(2.54)

In this, \( \beta \) is the collision frequency function, \( \nu \) is the particle volume, and \( f \) is particle size distribution function with volume the distributed variable. In the present work, four coagulation mechanisms, Brownian coagulation, mean shear coagulation, coagulation due to relative velocity between phases (also called kinematic coagulation) and turbulent coagulation, are considered.

For Brownian coagulation, mean shear coagulation, turbulent coagulation and velocity difference coagulation, the collision frequency functions are listed below. A
A detailed definition of these parameters is given in Section 2.1.

\[ \beta_b(r_k, r_i) = \frac{2kT}{3\mu} \left( \frac{1}{r_k} + \frac{1}{r_i} \right) (r_k + r_i) \]  
(2.55)

\[ \beta_s(r_k + r_i) = \frac{4}{3} (r_k + r_i) S \eta_{k,i} \]  
(2.56)

\[ \beta_t(r_k + r_i) = \frac{4}{3} \left( \frac{\varepsilon_d}{\nu} \right)^2 \]  
(2.57)

\[ \beta_r(r_k + r_i) = (r_k + r_i)^2 \Delta \vec{u} \eta_{k,i} \]  
(2.58)

The strain rate \( S \), turbulence dissipation rate \( \varepsilon_d \), and velocity difference term \( \Delta \vec{u} \) are defined as follows,

\[ S^2 = \left( \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \frac{\partial u_i}{\partial x_j} - \frac{2}{3} \frac{\partial u_k}{\partial x_k} \frac{\partial u_j}{\partial x_j} \]  
(2.59)

\[ \varepsilon_d = C_D \left( \frac{C_{\mu}}{C_D} \right) \Delta^2 S^3 \]  
(2.60)

\[ \Delta \vec{u} = \sqrt{(u_g - u_s)^2 + (v_g - v_s)^2 + (w_g - w_s)^2} \]  
(2.61)

In this, \( \Delta \) is a measure of the grid size, and \( C_{\mu} \) and \( C_D \) are constants (set equal to 0.01 and 1.0). The form for the turbulence dissipation rate is based on assuming equilibrium between turbulence production and its dissipation for a subgrid-scale process.

### 2.5.2 Sulfur dioxide chemical adsorption by limestone

Due to \( CaO \) and \( CaSO_4 \) being located in the same granule or particle (solids-1), a solids fraction \( X_{CaO} \) is used to distinguish the components. \( X_{CaO} \) is the mass fraction for \( CaO \) inside the solids-1, and \( 1 - X_{CaO} \) is the mass fraction for \( CaSO_4 \) inside solids-1. The source terms correspond to the one-step reaction in Equation 2.62 and are shown in Equation 2.63. It should be noted that source terms for mercury adsorption are added in Equation 2.63 for completeness. Precise forms for these are discussed in the next section.

\[ CaO(s) + \frac{1}{2} O_2(g) + SO_2(g) \rightarrow CaSO_4(s) \]  
(2.62)
\[ s_{g,2} = -M_{SO_2}R_{SO_2} \]
\[ s_{g,4} = -\frac{1}{2}M_{O_2}R_{SO_2} \]
\[ s_g = -M_{SO_2}R_{SO_2} - R_{Hg} - \frac{1}{2}M_{O_2}R_{SO_2} \] (2.63)
\[ s_{s,1}^x = -M_{CaO}R_{SO_2} \]
\[ s_{s,1} = -M_{CaO}R_{SO_2} + M_{CaSO_4}R_{SO_2} \]
\[ s_s = s_{s,1} + R_{Hg} \]

The reaction rate is obtained from Mattisson et al. [54,60] and is the same as in Equation 2.37 except that only fresh particles are considered \((\tau \rightarrow 0 \text{ in Equation 2.37})\).

\[ R_{SO_2} = \frac{\rho_s \alpha_s Y_{s,1} X_{CaO} C_1 \rho_g \alpha_g Y_{g,2} RT}{M_{CaO}} \frac{1000}{1000} \] (2.64)

The model constant \(C_1\) is a function of particle type and particle diameter [54,60] and is listed in Table 2.4.

\[ C_1 = A_1 + B_1 \left[ \log \left( \frac{d_p}{d_0} \right) \right]^{\alpha_1} \] (2.65)

where \(d_0\) is equal to 1 \(\mu m\) and \(d_p\) is the average sorbent particle diameter.

<table>
<thead>
<tr>
<th>(A_1 [s^{-1} kPa^{-1}])</th>
<th>Köping</th>
<th>Ignaberga</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-0.0033</td>
<td>0.039</td>
</tr>
<tr>
<td>(B_1 [s^{-1} kPa^{-1}])</td>
<td>0.48</td>
<td>-0.011</td>
</tr>
<tr>
<td>(\alpha_1 [-])</td>
<td>-4.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

### 2.5.3 Mercury vapor physical adsorption by activated carbon

The physical adsorption rate of elementary \(Hg\) onto activated carbon in Equation 2.40 can be written in a general form as

\[ -r_0 = C_0^{eff} C_0^{eff} \] (2.66)
where the coefficients $C_0^{eff}$ and $C_1^{eff}$ are listed in Table 2.5. Noting that $r_0$ is the initial rate of mercury uptake per unit mass of activated carbon (mmol Hg/sec·mg) and that $C_0$ is the vapor-phase mercury concentration (mmol Hg/L), the source term for the general transport equation then becomes:

$$s_{g,3} = -R_{Hg} = -\rho_s \alpha_{s,Y_{s,2}} C_0^{eff} \left( \frac{\rho_g \alpha_g Y_{g,3}}{1000 M_{Hg}} \right) C_1^{eff}$$

(2.67)

### Table 2.5: Constants for activated carbon

<table>
<thead>
<tr>
<th>Type</th>
<th>$C_0^{eff}$</th>
<th>$C_1^{eff}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPL</td>
<td>$1.09 \cdot 10^{-6}$</td>
<td>0.67</td>
</tr>
<tr>
<td>BPL-S</td>
<td>$1.12 \cdot 10^{-6}$</td>
<td>0.72</td>
</tr>
<tr>
<td>HGR</td>
<td>$1.66 \cdot 10^{-6}$</td>
<td>0.80</td>
</tr>
</tbody>
</table>
2.5.4 Summary

In summary, the source terms for the gas and solids phase continuity equations are listed below:

\[ s_{g,1} = -\kappa_s \alpha_s \rho_g \alpha_g Y_{g,1} \]
\[ s_{g,2} = -\frac{M_{SO_2}}{M_{CaO}} \rho_s \alpha_s Y_{s,1} X_{CaO} C_1 \frac{\rho_g \alpha_g Y_{g,2} RT}{1000} \]
\[ s_{g,3} = -\rho_s \alpha_s Y_{s,2} C^0_{eff} \left[ \frac{\rho_g \alpha_g Y_{g,3}}{1000 M_{R_g}} \right] C^1_{eff} \]
\[ s_{g,4} = -\frac{1}{2} \frac{M_{O_2}}{M_{CaO}} \rho_s \alpha_s Y_s X_{CaO} C_1 \frac{\rho_g \alpha_g Y_{g,2} RT}{1000} \]
\[ s_g = s_{g,2} + s_{g,3} + s_{g,4} \]
\[ s_{s,1} = s_{s,1} \left[ 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right] \]
\[ s_s = s_{s,1} - s_{g,3} \]
\[ s_{mtm,g,k} = u_{g,k} s_g \]
\[ s_{mtm,s,k} = u_{s,k} s_s \]

Due to the mass transfer between gas and solids phases, the related source terms also contribute to the time rate of change of momentum. Thus, the product \( u_{g,k} s_g \) is added to the source term of the \( k^{th} \) gas-phase momentum equation, and the product \( u_{s,k} s_s \) is added to the \( k^{th} \) solids-phase momentum equation.

\[ u_{g,1} = u_g, \ u_{g,2} = v_g, \ u_{g,3} = w_g \]
\[ u_{s,1} = u_s, \ u_{s,2} = v_s, \ u_{s,3} = w_s \]
3 Numerical Formulation

3.1 Preconditioning method

To enable time evolution and decrease numerical stiffness of the previous “gas mixture” and “solids mixture” system, artificial time derivatives of gas and solids pressure are added to the continuity and momentum equations. The modified equation system can be expressed in generalized coordinates as

\[ P \frac{\partial V}{\partial \tau} + \frac{\partial U}{\partial t} + \frac{\partial (F_k^* - F_v^*)}{\partial x_k} = S \]  

(3.1)

where preconditioning matrix \( P \), primitive variables \( V \) and \( W \), and the flux vectors \( F_k \) are listed as the following.

\[
P = \frac{1}{J} \begin{bmatrix}
0 & 0 & 0 & 0 & \frac{Y_{g1}}{\beta_g^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{Y_{g2}}{\beta_g^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{Y_{g3}}{\beta_g^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{Y_{g4}}{\beta_g^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{1}{\beta_g^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{u_{g1}}{\beta_g^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{u_{g2}}{\beta_g^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{u_{g3}}{\beta_g^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{u_{g4}}{\beta_g^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{w_{g1}}{\beta_g^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{w_{g2}}{\beta_g^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{w_{g3}}{\beta_g^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{w_{g4}}{\beta_g^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\rho_s a_s^2 Y_{s1} x_{CaQ}}{\beta_s^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\rho_s a_s^2 Y_{s1}}{\beta_s^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\rho_s a_s^2 s_{1}}{\beta_s^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\rho_s a_s^2 s_{2}}{\beta_s^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\rho_s a_s^2 s_{3}}{\beta_s^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\rho_s a_s^2 s_{4}}{\beta_s^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\rho_s a_s^2 w_{s1}}{\beta_s^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\rho_s a_s^2 w_{s2}}{\beta_s^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\rho_s a_s^2 w_{s3}}{\beta_s^2} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\rho_s a_s^2 w_{s4}}{\beta_s^2} & 0 & 0 & 0 & 0 & 0
\end{bmatrix}
\]  

(3.2)
where
\[
\frac{1}{\beta_g^2} = \frac{\rho_g}{\bar{\rho}} \left[ \frac{1}{\beta_g^2} - \frac{1}{a_s^2} \right]
\]
\[
\frac{1}{\beta_s^2} = \frac{\rho_s}{\bar{\rho}} \left[ \frac{1}{\beta_s^2} - \frac{1}{a_s^2} \right] \tag{3.3}
\]
\[
\frac{\partial \rho_g}{\partial \rho} = \frac{1}{a_g^2}
\]
\[
\frac{\partial \rho_s}{\partial \rho_s} = \rho_s a_s^2
\]

In this, \(\beta_g\) is a reference velocity for the gas phase, and \(\beta_s\) is a reference velocity for solids phase. The quantities \(\bar{\rho}\) and \(\bar{\rho}\) are reference densities, Edwards and Mao [97] and Mao et al. [98] found that the definition of these quantities had great influences on the results. The reasonable choices are listed from Equation 3.4 to Equation 3.6.

\[
\bar{\rho} = \bar{\rho} = \alpha_g \rho_g + \alpha_s \rho_s \tag{3.4}
\]
\[
\beta_g^2 = \min[a_g^2, \max(u_g^2 + v_g^2 + w_g^2, U_{ref,g}^2)] \tag{3.5}
\]
\[
\beta_s^2 = \min[a_s^2, \max(u_s^2 + v_s^2 + w_s^2, U_{ref,s}^2)] \tag{3.6}
\]

Both \(U_{ref,g}\) and \(U_{ref,s}\) are set to user-specified constants. The forms for \(\beta_g\) and \(\beta_s\) are consistent with the assumption of a compressible, but isothermal gas phase, and a “compressible” solids phase, in the sense that the solids phase can become more dense or dilute as conditions change. The preconditioning strategy for the solids phase replaces the solids sound speed by a quantity proportional to \(\beta_s\) as the degree of compaction increases. In contrast, a “supersonic flow” situation may prevail for dilute gas-solid flows, as the solids phase velocity may be much higher than the solids
sound speed. Other components are defined as follows.

\[
U = \frac{1}{J} \begin{bmatrix}
\rho_g \alpha_g Y_{g1} \\
\rho_g \alpha_g Y_{g2} \\
\rho_g \alpha_g Y_{g3} \\
\rho_g \alpha_g Y_{g4} \\
\rho_g \alpha_g u_g \\
\rho_g \alpha_g v_g \\
\rho_g \alpha_g w_g \\
\rho_s \alpha_s Y_{s,1} X_{CaO} \\
\rho_s \alpha_s Y_{s,1} \\
\rho_s \alpha_s \\
\rho_s \alpha_s u_s \\
\rho_s \alpha_s v_s \\
\rho_s \alpha_s w_s
\end{bmatrix}, \quad V = \begin{bmatrix}
Y_{g1} \\
Y_{g2} \\
Y_{g3} \\
Y_{g4} \\
p_g \\
v_g \\
w_g \\
X_{CaO} \\
Y_{s,1} \\
\alpha_s \\
u_s \\
v_s \\
w_s
\end{bmatrix}, \quad W = \begin{bmatrix}
Y_{g1} \\
Y_{g2} \\
Y_{g3} \\
Y_{g4} \\
p_g \\
v_g \\
w_g \\
X_{CaO} \\
Y_{s,1} \\
\alpha_s \\
u_s \\
v_s \\
w_s
\end{bmatrix}
\]

\[
F^{k,k=\xi,\eta,\zeta} = \frac{1}{J} \begin{bmatrix}
\rho_g \alpha_g \bar{U}_{g,k} Y_{g1} \\
\rho_g \alpha_g \bar{U}_{g,k} Y_{g2} \\
\rho_g \alpha_g \bar{U}_{g,k} Y_{g3} \\
\rho_g \alpha_g \bar{U}_{g,k} Y_{g4} \\
\rho_g \alpha_g \bar{U}_{g,k} u_g + \bar{k}_x p_g \\
\rho_g \alpha_g \bar{U}_{g,k} v_g + \bar{k}_y p_g \\
\rho_g \alpha_g \bar{U}_{g,k} w_g + \bar{k}_z p_g \\
\rho_s \alpha_s \bar{U}_{s,k} Y_{s,1} X_{CaO} \\
\rho_s \alpha_s \bar{U}_{s,k} Y_{s,1} \\
\rho_s \alpha_s \bar{U}_{s,k} \\
\rho_s \alpha_s \bar{U}_{s,k} u_s + \bar{k}_x p_s \\
\rho_s \alpha_s \bar{U}_{s,k} v_s + \bar{k}_y p_s \\
\rho_s \alpha_s \bar{U}_{s,k} w_s + \bar{k}_z p_s
\end{bmatrix}
\]

\[
F^{k,k=\xi,\eta,\zeta} = \frac{1}{J} \begin{bmatrix}
\rho_g \alpha_g \bar{U}^d_{g,k} Y_{g1} \\
\rho_g \alpha_g \bar{U}^d_{g,k} Y_{g2} \\
\rho_g \alpha_g \bar{U}^d_{g,k} Y_{g3} \\
\rho_g \alpha_g \bar{U}^d_{g,k} Y_{g4} \\
0 \\
T_{\xi_k,s} \\
T_{\eta_k,s} \\
T_{\zeta_k,s}
\end{bmatrix}
\]  \hspace{1cm} (3.8)

where

\[
\bar{U}_k = \bar{k}_x u + \bar{k}_y v + \bar{k}_z w, \quad \bar{k}_x = \frac{k_x}{|\nabla k|}, \quad \bar{k}_y = \frac{k_y}{|\nabla k|}, \quad \bar{k}_z = \frac{k_z}{|\nabla k|}.
\]  \hspace{1cm} (3.9)

\[
T_{ij} = \begin{bmatrix}
\xi_x \tau_{xx} + \xi_y \tau_{yx} + \xi_z \tau_{xz} \\
\xi_x \tau_{xy} + \xi_y \tau_{yy} + \xi_z \tau_{yz} \\
\xi_x \tau_{xz} + \xi_y \tau_{yz} + \xi_z \tau_{zz}
\end{bmatrix}
\]  \hspace{1cm} (3.10)
The eigenvalues of $P^{-1}A$, where $A = \frac{\partial F}{\partial V}$, are as the follows.

\[
\begin{align*}
\hat{U}_g, \quad \hat{U}_g, \quad \hat{U}_g, \quad \frac{1}{2} \left[ (1 + M_{ref,g}^2) \pm \sqrt{\hat{U}_g^2 (1 - M_{ref,g}^2) + \frac{4}{\alpha_g} a_g^2 M_{ref,g}^2} \right] \\
\hat{U}_s, \quad \hat{U}_s, \quad \hat{U}_s, \quad \frac{1}{2} \left[ (1 + M_{ref,s}^2) \pm \sqrt{\hat{U}_s^2 (1 - M_{ref,s}^2) + 4a_s^2 M_{ref,s}^2} \right]
\end{align*}
\] (3.11)

where

\[
\begin{align*}
\frac{1}{M_{ref,g}^2} &= 1 + \frac{1}{\rho_g} \frac{1 - M_g^2}{\rho M_g^2} \quad (3.12) \\
\frac{1}{M_{ref,s}^2} &= 1 + \frac{\rho_s}{\rho} \frac{1 - M_s^2}{M_s^2} \quad (3.13) \\
M_g^2 &= \frac{\beta_g^2}{a_g^2} \quad (3.14) \\
M_s^2 &= \frac{\beta_s^2}{a_s^2} \quad (3.15)
\end{align*}
\]

The eigenvalues corresponding to the gas and solids phases are similar to those typically resulting from preconditioning matrices of the forms proposed by Turkel [99], Choi and Merkle [100], and Weiss and Smith [101], among others, with specially defined reference Mach numbers given by Equations 3.12 and 3.13. These choices imply that numerical formulations discussed in Section 3.3 will be phase-coupled through the eigenvalues. The mixture gas sound speed can be obtained from the following equation.

\[
a_g^2 = R_{mixture} T = \left[ R \sum_{i=2}^M \frac{Y_{gi}}{M_{gi}} \right] T \quad (3.16)
\]
3.2 Implicit discrete representation

An implicit method is utilized to discrete Equation 3.1. The residual vector at time level \( n + 1 \) and subiteration \( l \) is given as

\[
R_{i,j,k}^{n+1,l} = \frac{U_{i,j,k}^{n+1,l} - U_{i,j,k}^{n}}{\Delta t} + \frac{(F - F_v)_{\xi, i+1/2,j,k}^{n+1,l} - (F - F_v)_{\xi, i-1/2,j,k}^{n+1,l}}{\Delta \xi} \\
+ \frac{(F - F_v)_{\eta, i,j+1/2,k}^{n+1,l} - (F - F_v)_{\eta, i,j-1/2,k}^{n+1,l}}{\Delta \eta} \\
+ \frac{(F - F_v)_{\zeta, i,j,k+1/2}^{n+1,l} - (F - F_v)_{\zeta, i,j,k-1/2}^{n+1,l}}{\Delta \zeta} - S_{i,j,k}^{n+1,l} \tag{3.17}
\]

where \( \Delta \xi, \Delta \eta, \) and \( \Delta \zeta \) are assumed to be unity for convenience. This may be linearized in an Euler implicit fashion to yield

\[
\left[ \frac{P + M}{\Delta t} + M \frac{\partial}{\partial V} \left( \frac{\partial F_\xi}{\partial \xi} \right) + \frac{\partial}{\partial V} \left( \frac{\partial F_\eta}{\partial \eta} \right) \right. \\
\left. + \frac{\partial}{\partial V} \left( \frac{\partial F_\zeta}{\partial \zeta} \right) - \frac{\partial S}{\partial V} \right] \frac{\partial V}{\partial W} \Delta W_{i,j,k}^{n+1,l} = -R_{i,j,k}^{n+1,l} \tag{3.18}
\]

where \( M = \frac{\partial U}{\partial W} \). The algebra equations can be written in the following way.

\[
A_1(\Delta W)_{i-1,j,k}^{n+1,l} + A_2(\Delta W)_{i,j-1,k}^{n+1,l} + A_3(\Delta W)_{i,j,k-1}^{n+1,l} + A_4(\Delta W)_{i,j,k}^{n+1,l} \\
+ A_5(\Delta W)_{i,j,k+1}^{n+1,l} + A_6(\Delta W)_{i,j+1,k}^{n+1,l} + A_7(\Delta W)_{i+1,j,k}^{n+1,l} = -R_{i,j,k} \tag{3.19}
\]

where

\[
A_1 = -\frac{1}{2} \left[ A_{\xi, i-1,j,k} + |\Lambda_\xi| B_{i-1/2,j,k} \right] \\
A_2 = -\frac{1}{2} \left[ A_{\eta, i,j-1,k} + |\Lambda_\eta| B_{i,j-1/2,k} \right] \\
A_3 = -\frac{1}{2} \left[ A_{\zeta, i,j,k-1} + |\Lambda_\zeta| B_{i,j,k-1/2} \right] \\
A_4 = \frac{1}{2} \left[ C_{i,j,k} + |\Lambda_\xi| B_{i-1/2,j,k} + |\Lambda_\eta| B_{i,j-1/2,k} + |\Lambda_\zeta| B_{i,j,k-1/2} \right. \\
\left. + |\Lambda_\zeta| B_{i,j,k+1/2} + |\Lambda_\eta| B_{i,j,k+1/2} + |\Lambda_\zeta| B_{i+1/2,j,k} \right] \\
A_5 = +\frac{1}{2} \left[ A_{\zeta, i,j,k+1} - |\Lambda_\zeta| B_{i,j,k+1/2} \right] \\
A_6 = +\frac{1}{2} \left[ A_{\eta, i,j+1,k} - |\Lambda_\eta| B_{i,j+1/2,k} \right] \\
A_7 = +\frac{1}{2} \left[ A_{\xi, i+1,j,k} - |\Lambda_\xi| B_{i+1/2,j,k} \right] \tag{3.20}
\]
\[ A_{m, i, j, k} = \left[ \frac{\partial F^{m, m=\xi, \eta, \zeta}}{\partial V} \frac{\partial V}{\partial W} \right]_{i, j, k} \]
\[ B_{i, j, k} = \left[ (P + M) \frac{\partial V}{\partial W} \right]_{i, j, k} \]
\[ C_{i, j, k} = \left[ \frac{P + M}{\Delta \tau} + \frac{M}{\Delta t} - \partial S \frac{\partial V}{\partial W} \right]_{i, j, k} \]
\[ \Lambda_k = \begin{bmatrix} \lambda_{g,k} & 0 \\ 0 & \lambda_{s,k} \end{bmatrix} \] (3.21)

Detailed information about the matrices and eigenvalues are listed in the appendices. This implicit system is approximately solved at each pseudo-time step to yield an update to the solution vector \( W \): 
\[ W^{n+1,l+1} = W^{n+1,l} + \Delta W^{n+1,l} \]. An incomplete LU decomposition method is used in this regard. Typically, 8 to 20 subiterations are required each physical time step to ensure temporal accuracy.

### 3.3 Low-diffusion flux-splitting scheme (LDFSS)

Earlier works [102, 103] have detailed the development of LDFSS (low diffusion flux splitting scheme), an upwinding technique that combines the the robustness and simplicity of flux-vector splitting methods with the accuracy of flux-difference splitting methods. General procedures for extending this method to low-Mach gas-phase flows have been presented by Edwards and Liou in [103] and extensions suitable for real fluids undergoing equilibrium phase transitions have been presented by Edwards et al. in [104].

The present work presents extensions of LDFSS for the gas-solid system discussed above. The formulation follows from the low-Mach and real-fluid extensions of Edwards et al. [103] and [104].

The interface flux vector \( F \) in equation 3.1 is split into phasic contributions
\[ F_g + F_s: \]

\[
F = \begin{bmatrix}
\rho_g \alpha_g \bar{u}_g Y_{g,i} \\
\rho_g \alpha_g \bar{u}_g \\
\rho_g \alpha_g \bar{u}_g^2 + \bar{p}_g \\
\rho_g \alpha_g \bar{u}_g \bar{v}_g \\
\rho_g \alpha_g \bar{u}_g \bar{w}_g \\
0 \\
0 \\
0 \\
0 \\
0
\end{bmatrix} + \begin{bmatrix}
0 \\
0 \\
0 \\
0 \\
0 \\
\rho_s \alpha_s \bar{u}_s Y_{s,j} \\
\rho_s \alpha_s \bar{u}_s \\
\rho_s \alpha_s \bar{u}_s^2 + \bar{p}_s \\
\rho_s \alpha_s \bar{u}_s \bar{v}_s \\
\rho_s \alpha_s \bar{u}_s \bar{w}_s
\end{bmatrix}
\tag{3.22}
\]

where \( Y_{g,i} \) stands for \( i \)-th gas species, and \( Y_{s,j} \) stands for \( j \)-th solids species.

Each phasic contribution \( F_k \) (\( k = \text{gas or solids} \)), evaluated at a cell interface, is then further split into convective and pressure contributions \( F_{k,1/2} = F_{k,1/2}^c + F_{k,1/2}^p \), which are discretized separately as:

\[
F_{k,1/2}^c = U_k^+ \begin{bmatrix}
\rho_k \alpha_k \bar{Y}_{k,i} \\
\rho_k \alpha_k \\
\rho_k \alpha_k \bar{u}_k \\
\rho_k \alpha_k \bar{v}_k \\
\rho_k \alpha_k \bar{w}_k
\end{bmatrix} + U_k^- \begin{bmatrix}
\rho_k \alpha_k \bar{Y}_{k,i} \\
\rho_k \alpha_k \\
\rho_k \alpha_k \bar{u}_k \\
\rho_k \alpha_k \bar{v}_k \\
\rho_k \alpha_k \bar{w}_k
\end{bmatrix}
\tag{3.23}
\]

and

\[
F_{k,1/2}^p = \begin{bmatrix}
0 \\
0 \\
p_{k,1/2} \\
0 \\
0
\end{bmatrix}
\tag{3.24}
\]

LDFSS is grounded in the concept of a “numerical speed of sound” [105] that facilitates the shift from a discretization suitable for strongly compressible flows to one suitable for incompressible flows. Two numerical sound speeds, each associated with a particular phase and developed from the acoustic eigenvalues, are defined as:

\[
\tilde{a}_{g,1/2} = \left( \frac{\sqrt{u_g^2(1 - M_{\text{ref},g}^2) + \frac{4}{\alpha_g} u_g^2 M_{\text{ref},g}^2}}{1 + M_{\text{ref},g}^2} \right)^{1/2}
\tag{3.25}
\]

\[
\tilde{a}_{s,1/2} = \left( \frac{\sqrt{u_s^2(1 - M_{\text{ref},s}^2) + 4\alpha_s^2 M_{\text{ref},s}^2}}{1 + M_{\text{ref},s}^2} \right)^{1/2}
\tag{3.26}
\]
Quantities appearing in 3.25 and 3.26 are defined in the following and are arithmetically-averaged to the cell interface. Other quantities needed in the LDFSS formulations are phasic Mach numbers at left (L) and right (R) states:

\[ M_{k,L/R} = \frac{u_{k,L/R}}{a_{k,1/2}}, \]  

(3.27)

and polynomials in Mach number [106]:

\[ M_{(1),k}^\pm = \frac{1}{2} (M_k \pm |M_k|), \]  

(3.28)

\[ M_{(2),k}^\pm = \begin{cases} \pm \frac{1}{4} (M_k \pm 1)^2, & |M_k| < 1 \\ M_{(1),k}^\pm, & \text{otherwise} \end{cases}, \]  

(3.29)

\[ M_{(4),k}^\pm = \begin{cases} \pm \frac{1}{8} (M_k \pm 1)^2 \pm \frac{1}{3}(M_k^2 - 1)^2, & |M_k| < 1 \\ M_{(1),k}^\pm, & \text{otherwise} \end{cases}, \]  

(3.30)

The numerals in the subscripts of \( M \) indicate the degree of the polynomials.

From this, \( U_k^\pm \) is defined for LDFSS as:

\[ U_k^+ = \tilde{a}_{k,1/2}(M_{(2),k,L}^+ M_{(1),k}^+) \]  

(3.31)

\[ U_k^- = \tilde{a}_{k,1/2}(M_{(2),k,R}^- + M_{(1),k}^-), \]  

(3.32)

where

\[ M_{1/2}^+ = M_{1/2}(1 - \frac{\Delta p_k}{2\rho_k \alpha_{k,L} V_{ref,1/2}^2}) \]  

(3.33)

\[ M_{1/2}^- = M_{1/2}(1 + \frac{\Delta p_k}{2\rho_k \alpha_{k,R} V_{ref,1/2}^2}) \]  

(3.34)

and

\[ \Delta p_k = p_{k,L} - p_{k,R} \]  

(3.35)

The notation \( M_{(2),k,L}^+ \) (for example) indicates the evaluation of the polynomial (3.29) using the phasic Mach number \( M_k \) at the left state. The function \( M_{1/2} \) is given as

\[ M_{1/2} = \frac{1}{2} \left[ M_{(2),k,L}^+ M_{(1),k,L}^+ - M_{(2),k,R}^- - M_{(1),k,R}^- \right] \]  

(3.36)
The function $V_{ref}^2$ is equal to $\frac{a_{\rho}^2}{\alpha_{\rho}} M_{ref,g}^2$ for the gas phase and $a_{\alpha}^2 M_{ref,s}^2$ for the solids phase.

For the pressure splitting, a general Van Leer / Liou-type polynomial splitting is defined for phase $k$ as:

$$p_{k,1/2} = \mathcal{P}_{(m),k,L}^+ p_{k,L} + \mathcal{P}_{(m),k,R}^- p_{k,R}$$  \hspace{1cm} (3.37)

where $m = 1, 3, \text{ or } 5$ corresponds to polynomials of different degrees, defined as:

$$\mathcal{P}_{(1),k}^{\pm} = \begin{cases} \frac{1}{2} (1 \pm M_k), & |M_k| < 1 \\ \frac{1}{M_k} M_{(1),k}^{\pm}, & \text{otherwise}, \end{cases}$$  \hspace{1cm} (3.38)

$$\mathcal{P}_{(3),k}^{\pm} = \begin{cases} M_{(2),k}^{\pm} (\pm 2 - M_k), & |M_k| < 1 \\ \frac{1}{M_k} M_{(1),k}^{\pm}, & \text{otherwise}, \end{cases}$$  \hspace{1cm} (3.39)

$$\mathcal{P}_{(5),k}^{\pm} = \begin{cases} M_{(2),k}^{\pm} [(\pm 2 - M_k) \\ \mp 3 M_k, M_{(2),k}^{\pm}], & |M_k| < 1 \\ \frac{1}{M_k} M_{(1),k}^{\pm}, & \text{otherwise}, \end{cases}$$  \hspace{1cm} (3.40)

Equation 3.37 can be rewritten without approximation as

$$p_{k,1/2} = \frac{1}{2} (\mathcal{P}_{(m),k,L}^+ - \mathcal{P}_{(m),k,R}^-) (p_{k,L} - p_{k,R})$$

+ \frac{1}{2} (p_{k,L} + p_{k,R}) (\mathcal{P}_{(m),k,L}^+ + \mathcal{P}_{(m),k,R}^-)$$  \hspace{1cm} (3.41)

which can be further separated into cell-average plus diffusive components:

$$p_{k,1/2} = \frac{1}{2} (p_{k,L} + p_{k,R})$$

+ \frac{1}{2} (\mathcal{P}_{(m),k,L}^+ - \mathcal{P}_{(m),k,R}^-) (p_{k,L} - p_{k,R})$$

+ \frac{1}{2} (p_{k,L} + p_{k,R}) (\mathcal{P}_{(m),k,L}^+ + \mathcal{P}_{(m),k,R}^- - 1)$$  \hspace{1cm} (3.42)

The third term on the right-hand side of (3.42) is the major problem: when the polynomials are evaluated using the phasic Mach numbers, the term may be excessively large for low-Mach flows. A better scaling, one also valid for real fluids, is found
by replacing \( \frac{1}{2} (p_{k,L} + p_{k,R}) \) in this term by \( \rho_k V_{ref,1/2}^2 \). The final form of the pressure splitting is thus

\[
\begin{align*}
p_{k,1/2} &= \frac{1}{2} (p_{k,L} + p_{k,R}) \\
&+ \frac{1}{2} (p_{(m),k,L}^+ - p_{(m),k,R}^-) (p_{k,L} - p_{k,R}) \\
&+ \rho_k V_{ref,1/2}^2 (p_{(m),k,L}^+ + p_{(m),k,R}^- - 1)
\end{align*}
\] (3.43)

The current implementation for LDFSS uses the first-degree polynomials \( P_{(1),k}^\pm \) exclusively. It is extended to second order to improve the accuracy of the solution. The second order extension is accomplished by a slope-limited, upwind-biased interpolation of the primitive variable vector \( V \) to the interface, using TVD-type methods to eliminate unwanted oscillations [107, 108]. The Van-Leer limiter and minmod limiter are used for the samples presented in this study. \( q \) is chosen to be an arbitrary quantity which will be interpolated to the left and right states. Then the interpolations can be expressed as:

\[
\begin{align*}
q_L &= q_i + P_i^l \varphi (q_{i+1} - q_i, q_i - q_{i-1}) \\
q_R &= q_{i+1} - P_{i+1}^l \varphi (q_{i+2} - q_{i+1}, q_{i+1} - q_i)
\end{align*}
\] (3.44, 3.45)

where \( P_i^l \) is a pressure limiter and \( \varphi \) is an averaging procedure. The solids pressure limiter \( P_i^l \) is defined as

\[
P_i^l = \frac{1}{2} \left[ 1.0 - \frac{\frac{1}{2} |P_{i+1,s} - P_{i-1,s}| + 1000.0 \times \alpha_{s,max}}{\frac{1}{2} |P_{i+1,s} - P_{i-1,s}|} \right]
\] (3.46)

\[
\begin{align*}
\varphi_{mnd} (x, y) &= \text{sign} (1.0, x) \max [0.0, \min (x \times \text{sign} (1.0, y), y \times \text{sign} (1.0, x))] \\
\varphi_{VL} (x, y) &= \frac{y \times |x| + x \times |y|}{|x| + |y|}
\end{align*}
\] (3.47)

where \( \varphi_{mnd} \) and \( \varphi_{VL} \) are minmod and Van Leer limiter, respectively.
3.4 MPI and parallelization

The calculation of flows within complex domains using structured grids usually requires some type of domain-decomposition strategy. Domain decomposition involves the partitioning of a complex domain into simpler subdomains, which may be solved in sequence or in parallel. The 3-D calculations were run in parallel on the IBM SP-2 at the North Carolina Supercomputering Center (NCSC).

3.5 Boundary conditions

Three kinds of boundary conditions are used in the present work: inlet, outlet and wall. For the inlet, mass fractions for gas species are fixed, gas and solids voidage fractions are extrapolated from interior cells, and the superficial velocities for the gas and solids are fixed. The pressure is extrapolated from the interior cells. For the outlet, all variables, excepting the pressure, are extrapolated from interior cells. The pressure is fixed to atmosphere pressure for the calculations presented in this study. A slip-wall condition is used for the solids phase, meaning that the solids flow at the wall is everywhere tangent to the wall. For the gas-phase, either a slip-wall condition or a non-slip wall condition (velocities set to zero) is used, depending on the case.
4 Results and Discussion

In this section, the methods outlined earlier are tested for several problems in fluidization. The first problem is that of jet-induced bubble formation in a minimally fluidized bed. Both two-dimensional and three-dimensional cases are considered. The second is a three-dimensional circulating fluidized bed. The third is downward-moving fluidized bed. The final problem is simulation of fine PM agglomeration, sulfur dioxide chemical adsorption and mercury vapor physical adsorption inside a prototype CFBA reactor [using “gas mixture” and “solids mixture” model].

Only the last problem is solved for a compressible gas, the first three assume an incompressible gas. In this, the sound speed $a_g$ is set to a very large value ($10^{10}$) and the gas density is held constant. Table 4.1 shows the grid and simulation parameters for the above samples.

<table>
<thead>
<tr>
<th>sample</th>
<th>grid ($x \times y \times z$)</th>
<th>$\Delta t$</th>
<th>CFL</th>
<th>computer</th>
<th>block</th>
<th>nodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-D bubble</td>
<td>$65 \times 65$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>2.5</td>
<td>Microway</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3-D bubble</td>
<td>$65 \times 65 \times 65$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>2.5</td>
<td>IBM SP</td>
<td>$4 \times 4 \times 4$</td>
<td>64</td>
</tr>
<tr>
<td>CFBAs</td>
<td>$33 \times 33 \times 201$</td>
<td>$5.0 \times 10^{-4}$</td>
<td>2.5</td>
<td>IBM SP</td>
<td>$1 \times 1 \times 40$</td>
<td>40</td>
</tr>
<tr>
<td>DFB</td>
<td>$121 \times 3 \times 81$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>2.5</td>
<td>IBM SP</td>
<td>$12 \times 1 \times 4$</td>
<td>48</td>
</tr>
<tr>
<td>“mixture” CFBA</td>
<td>$21 \times 21 \times 201$</td>
<td>$2.0 \times 10^{-4}$</td>
<td>2.5</td>
<td>IBM SP</td>
<td>$1 \times 1 \times 40$</td>
<td>40</td>
</tr>
</tbody>
</table>

4.1 Bubble bed simulations

4.1.1 2-D bubble bed simulations

For the two-dimensional simulations, a rectangular $0.39 \times 0.58$ m domain containing $65 \times 65$ mesh points is utilized. Detailed information is listed in Table 4.2. Nominal initial conditions are:
0 ≤ z ≤ h_{bed}, \quad \alpha_g = 0.44
0 \leq x \leq 0.39 \quad \alpha_s = 0.56
u_g = 0
\alpha_g v_g = 0.28 \text{ m/s}
u_s = 0
v_s = 0
p_g = p_\infty + \rho_s \alpha_s g (h_{bed} - z)

h_{bed} < z < 0.58, \quad \alpha_g = 0.999
0 \leq x \leq 0.39 \quad \alpha_s = 0.001
u_g = 0
\alpha_g v_g = 0.28 \text{ m/s}
u_s = 0
v_s = 0
p_g = p_\infty

Table 4.2: Parameters for bubble bed

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>particle diameter</td>
<td>500 \mu m</td>
</tr>
<tr>
<td>particle density</td>
<td>2660 kg/m³</td>
</tr>
<tr>
<td>gas density</td>
<td>1.235 kg/m³</td>
</tr>
<tr>
<td>gas viscosity, \mu</td>
<td>$20 \times 10^{-6}$ kg/(m·s)</td>
</tr>
<tr>
<td>outlet pressure, p_\infty</td>
<td>101 000 Pa</td>
</tr>
<tr>
<td>minimum superficial gas velocity, \alpha_g v_g</td>
<td>0.28 m/s</td>
</tr>
<tr>
<td>superficial gas jet velocity</td>
<td>5.77 m/s</td>
</tr>
<tr>
<td>width of bed</td>
<td>0.39 m</td>
</tr>
<tr>
<td>jet width</td>
<td>0.0127 m</td>
</tr>
</tbody>
</table>

For these conditions, a minimum fluidization velocity of \( u_{mf} = 0.64 \text{ m/s} \) is obtained [23], as is a minimum superficial fluidization velocity of \( \alpha_g u_{mf} = 0.28 \text{ m/s} \).

Nominal boundary conditions are:

\[
0 \leq z \leq 0.58, \quad \alpha_s \text{ extrapolated from interior}
\]
\[
x = 0, x = 0.39 \quad p_g \text{ extrapolated from interior}
\]
\[
u_g = 0
\]
\[
v_g \text{ extrapolated from interior}
\]
\[
u_s = 0
\]
\[
v_s \text{ extrapolated from interior}
\]
Figure 4.1: Experimental bubble by Gidaspow

Figure 4.2: Numerical bubble by Gidaspow
Figure 4.3: Effect of grid size on two-dimensional bubble shape
$0 < x < 0.39$, $\alpha_s$ extrapolated from interior
$z = 0$ $p_g$ extrapolated from interior
$u_g = 0$
$\alpha_g v_g = 0.28 \text{ m/s}$
$u_s$ extrapolated from interior
$v_s = 0$

$0 < x < 0.39$, $\alpha_s$ extrapolated from interior
$z = 0.58$ $p_g = p_\infty$
$u_g$ extrapolated from interior
$v_g$ extrapolated from interior
$u_s$ extrapolated from interior
$v_s = 0$

These boundary conditions are applied at a cell interface using an array of ghost cells placed outside the physical domain and standard finite-volume strategies. The exception is the gas pressure at the inflow ($z = 0$) boundary. Here, it is necessary to linearly extrapolate the gas pressure to the ghost cell to preserve the proper pressure-height relation.

The schemes are extended to second-order accuracy using standard slope-limiting procedures applied to the primitive variable vector $V$. The Van Leer limiter is used in the results that follow. The two-dimensional simulations are advanced in time using a fixed time step of $1 \times 10^{-4}$ seconds, with 25 subiterations performed per time step. Larger numbers of subiterations changed the results only minimally. Reference velocities ($U_{\text{ref},g}$, $U_{\text{ref},s}$) for both phases are set to 5 m/s, and $C_s = 0.02$.

Figure 4.1 is experimental bubble by Gidaspow et al. [82], Figure 4.2 is their simulation result, and Figure 4.3 is our present simulation results. Good agreement with the bubble shape is indicated, and the predictions also show an inception bubble at the bottom of the bed. Figure 4.3 also provides the subsequent bubble evolution history; including formation, growth and burst stages. Solids can be found in the tail vortex of the bubble. Bubble evolution induces particle backmixing. It can be found that grid size has influence on bubble shape. The use of fine grid ($129 \times 129$)
results in a rapid breakdown and a rather chaotic bubble bed with more evidence of
fine-scale structure, but the general trends are as evidenced in the coarse-grid results.

The effects of reference velocity, $C_s$, spatial accuracy (1st order, Van Leer limiter,
Superbee limiter) and choice of pressure splitting on bubble shape are studied in detail
in [98].

4.1.2 3-D bubble bed simulations

The three-dimensional algorithm is developed as a straightforward extension of the
two-dimensional schemes and is parallelized for use on the North Carolina Super-
computing Center’s IBM-SP2 using a MPI message-passing/domain-decomposition
strategy.

Parameters for simulation of three-dimensional bubble formation in a fluidized
bed are the same as those listed above, except for: $d_p$ (particle diameter) = 800 $\mu$m,
and $\rho_s = 2420$ kg/m$^3$. The geometry is a 0.39 m $\times$ 0.39 m $\times$ 0.58 m rectangular
box containing 65 $\times$ 65 $\times$ 65 grid points, uniformly spaced in each direction. Nominal
initial and boundary conditions are the same as mentioned earlier, except for the
addition of slip surfaces corresponding to the third direction. A 5.77 m/s jet of
air, exiting through a 0.0127 $\times$ 0.0127 m square opening in the middle of the bottom
plate, initiates bubble formation. Figure 4.4 presents snapshots of solids void fraction
along constant X, Y, and Z planes at different times after jet injection. As before,
the initial response is the formation of a gas bubble which subsequently grows, then
collapses near the end of the bed in 4.4-a and 4.4-b. After each subsequent bubble
event, solids are entrained into the region occupied by the bubble, pinching off the jet
and leading to the formation of a periodic sequence of smaller bubbles that eventually
pass through the bed surface (Figures 4.4-c and 4.4-d). As in the two-dimensional
case, a spouting behavior is observed at later times (Figures 4.4-d, 4.4-e, and 4.4-f).
The LDFSS scheme, combined with the Van Leer limiter, captures the different stages
Figure 4.4: Snapshots of solids voidage in simulation of 3-D fluidized bed
of three-dimensional bubble formation with good resolution of gas-solid interfaces.

4.2 Gas/solids two phase flow simulation in circulating fluidized bed

This test case corresponds to an experiment of Van den Moortel, et al. [109] involving gas-solid flow within the riser section of a circulating fluidized bed. Prior computational results for this case have been presented by Zhang and VanderHeyden [85] using a similar hydrodynamics model and an Arbitrary Lagrangian / Eulerian (ALE) numerical method. The geometry is adapted from Zhang and VanderHeyden [85] and consists of a 2 m vertical riser with a $0.2 \times 0.2$ m cross-sectional area. The cross-sectional area is linearly shrunk to $0.1 \times 0.1$ m above 1.8 m. The calculation is initialized with 3% solids voidage, uniformly distributed within the riser. Other parameters are: $d_p$ (particle diameter) = 120 $\mu$m, $\rho_s = 2400$ kg/m$^3$, $\rho_g = 1.200$ kg/m$^3$, $\mu = 18 \times 10^{-6}$ kg/(m-s), and $p_\infty = 101000$ Pa. As the iteration progresses, the solids mass flow rate calculated at the outflow is imposed at a vertical inflow plane ($0.2 \times 0.05$ m) at the bottom of the riser, thus simulating the recycling of the solids. After an initial period of time, the time-dependent solution reaches a statistically stationary state, characterized by a constant time-averaged solids mass flow rate.

Figure 4.5 shows snapshots of the logarithm of the solids void fraction during the start-up period and after the system reaches a statistically steady state. The key features of the flow field are elongated mesoscale structures containing higher solids concentrations. As expected, the solids voidage is highest near the bottom of the riser and near the walls, though a distinct core-annulus structure is not present. The LDFSS scheme (with $U_{ref,g} = U_{ref,s} = 15$ m/s) is clearly capable of capturing the fine-scale features of this complex flow field. Figure 4.6 shows the clusters and streamers, which are induced by inelastic collisions between particles and are associated with relative motion between gas and solids particles. Solids particles are set uniformly
Figure 4.5: Snapshots of solids voidage in simulation of 3-D circulating fluidized bed
Figure 4.6: Snapshots of meso-structure in x-z plane of CFBA
Figure 4.7: Experimental meso-structure in dilute suspension riser by Tsukada [1] distributed inside the CFBA initially. With the development of gas jet at the bottom and side inlet section, the superficial gas velocity becomes larger enough to support them, then the statistically steady state arrives. Agrawal [110] utilized a complex kinetic model considering granular temperature and solids stress for a very simple two-dimensional geometry and used a very fine grid (1 cm x 4 cm with 16 x 64 cells) to arrive at the solution presented in Figure 4.8. Our mesh spacing is around 10 times larger than theirs, but it can also simulate macro-scale solids clusters and streamers. Tsukada [1] utilized laser sheet image to measure the clusters (brighter part) and gas pockets shown in Figure 4.7. It can be found that Figure 4.6 is closer to experimental results shown in Figure 4.7 than that of Agrawal et al. [2]. In Figure 4.9, we plot the particle mass flux as a function of time for the case of superficial gas velocity equal to 1.0 m/s. It can be found the statistically steady state appear after 3 seconds. Data for statistics are collected after the initial transients are expelled. Figure 4.10 compares average solids mass flux (referenced to the riser cross-sectional area) with experimental data, and it can be found that Van Leer limiter generates better results than the minmod limiter since it is less dissipative. Figures 4.11 and 4.12 compare average solids vertical velocity at $z/H = 0.5$ and $z/H = 0.6$, respectively, with experimental
Figure 4.8: Meso-structure simulated by Agrawal et al. [2]
Figure 4.9: Time series of particle mass flux

Figure 4.10: Average mass flux at statistically steady state
Figure 4.11: Particle vertical velocity profile at height $z/H = 0.5$

Figure 4.12: Particle vertical velocity profile at height $z/H = 0.6$
Figure 4.13: Standard deviation of particle vertical velocity at height $z/H = 0.5$

Figure 4.14: Averaged solid volume fraction along the height
data and predictions of Zhang and VanderHeyden [85]. The computational predictions for vertical velocity are very similar. Agreement with experimental vertical velocity data is only fair but as noted in Zhang and VanderHeyden [85], the experimental profiles may not be consistent with the preservation of a constant solids mass flow rate at the statistically steady state. Figure 4.13 provides the standard deviation of particle vertical velocity. It is interesting to note that the fluctuations in particle velocity are of the same order as the mean velocity in the experiment and in both simulations. Figure 4.14 shows exponential distribution of solids voidage fraction inside the fluidized bed. It is very dense within 0.25 meters from the bottom and very dilute above 0.5 meters.

### 4.3 Circulating downward fluidized bed

A Circulating Downward Fluidized Bed (CDFB) has many advantages such as good gas-solids contact, less gas-solids backmixing, a short contact time and more uniform RTD, compared with the upward-flowing fluidized bed (riser) [111–114]. These properties are particularly beneficial to the processes of fluidized catalytic cracking (FCC) and residual oil fluidized catalytic cracking (RFCC) where extremely short but uniform contact times between gas and solids are required [115]. But how to choose or control the operating parameters for the CDFB operation is less understood than for the traditional fluidized bed. This section tests the performance of the numerical method in capturing key features of the CDFB.

Figure 4.15 shows the initial condition for a CDFB simulation. Initially, all particles are set at the top of the CDFB. They then will fall down due to gravity and will exit the bottom, and then be recycled to the top. Triangles are obstacles inside the downward fluidized bed. In order to circulate, the particle flow rate at the top is set to be equal to that at the bottom as done before. Figure 4.16 shows the snapshot when
Figure 4.15: Particle initial position in the (Circulating) DFB

Figure 4.16: A snapshot within the CDFB with superficial gas velocity $U_{mf}$
Figure 4.17: A snapshot within the CDFB with superficial gas velocity $0.1U_{mf}$

Figure 4.18: Final shape of solids in the DFB
the superficial gas velocity is equal to minimum fluidization velocity. Bubbles are found inside the circulating DFB, which is not desirable for DFB because of particles mixing. Due to consecutive and/or side reaction, back mixing leads to a decrease in selectivity and yield. However, when the superficial gas velocity decreases to $0.1U_{mf}$, bubble disappears as shown in Figure 4.17. Figure 4.18 shows the “wave” surface shape when particles fall down freely through triangle obstacles and accumulate at the bottom when the superficial gas velocity is negligible ($10^{-4}U_{mf}$).

### 4.4 Gas mixture and solids mixture simulation in a prototype circulating fluidized bed adsorber

The “gas mixture” and “solids mixture” model described earlier is utilized to simulate fine particulate matter agglomeration, sulfur dioxide chemical adsorption and mercury vapor physical adsorption in a circulating fluidized bed. The geometry is the same as in Section 4.2, but the flow conditions are changed to be more representative of the flue gas condition upstream of a particulate collection device. These are representative of flue gas generated by coal combustion [116] and are listed in Table 4.3.

Figure 4.19 and 4.20 show snapshots of sorbent solids species after 1 second and 5.5 seconds of operation, respectively. Solids clusters and streamers can be seen from the solids voidage fraction contours. After 5.5 seconds of operation, the reactor has reached a statistically steady state, which can also be seen in Figure 4.28. The mass fraction of $CaO$ (related to the mass of solids-1) decreases due to the chemical reaction between $CaO$ and $SO_2$. For example, the initial value of $X_{CaO}$ is 0.01, and it decreases around 0.0079 after 5.5 seconds of operation. The overall mass fraction of solids-1, relative to the total solids mass, increases, however, due to adsorption of $O_2$ and $SO_2$ and the formation of $CaSO_4$. For example, the value of $Y_{s1}$ increases from initially 0.999 to about 0.999003 after 5.5 seconds of operation.

It should be noted that it is the inert gas that enters the riser through the side
Table 4.3: Initial gas and solids species mass fraction

<table>
<thead>
<tr>
<th>species</th>
<th>composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>4.63e-1</td>
</tr>
<tr>
<td>$SO_2$</td>
<td>1.14e-1</td>
</tr>
<tr>
<td>$Hg$</td>
<td>7.34e-9</td>
</tr>
<tr>
<td>$O_2$</td>
<td>1.48e-1</td>
</tr>
<tr>
<td>$H_2O$</td>
<td>7.22e-2</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>2.03e-1</td>
</tr>
<tr>
<td>fine PM</td>
<td>1.0 (normalized)</td>
</tr>
<tr>
<td>$\alpha_s$</td>
<td>0.03</td>
</tr>
<tr>
<td>$Y_{s,1}$</td>
<td>0.999</td>
</tr>
<tr>
<td>$Y_{s,2}$</td>
<td>0.001</td>
</tr>
<tr>
<td>$X_{CaO}$</td>
<td>1.0e-2</td>
</tr>
<tr>
<td>$X_{CaSO_4}$</td>
<td>0.99</td>
</tr>
<tr>
<td>$\rho_{AC}$</td>
<td>1500 kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_{CaO}$</td>
<td>2400 kg/m$^3$</td>
</tr>
<tr>
<td>$\rho_{CaSO_4}$</td>
<td>3000 kg/m$^3$</td>
</tr>
<tr>
<td>$V_{superficial}$</td>
<td>1.1 m/s</td>
</tr>
<tr>
<td>$d_p$</td>
<td>120.0e-6 m</td>
</tr>
<tr>
<td>$\mu_g$</td>
<td>18.0e-6 kg/(m-s)</td>
</tr>
<tr>
<td>Schmidt number</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Figure 4.19: A snapshot for solids species at 1.0 seconds

Figure 4.20: A snapshot for solids species at 5.5 seconds
Figure 4.21: Average solids fraction distribution along the height of CFBA

Figure 4.22: Average gas species along the height of CFBA
inlet of the riser. Thus, there is some slight dilution that is more pronounced in
the snapshots corresponding to 0.5 seconds of operation. The location with very low
concentration for reactive gas species at the inlet side close to the bottom is caused
by inert gas injection.

The temperature is fixed at 413 K degree in the present study. This is lower
than the temperature range for which the \( SO_2 \) uptake model was developed [850\(^\circ\)C],
so the \( SO_2 \) conversion results may not be correct. The mercury vapor adsorption
experiments were conducted at 413 K.

Figure 4.21 and Figure 4.22 show the average solids voidage fraction, normalized
gas species concentration, and fine PM number density along the riser height. They
are line-averaged in the center plane (\( y = 0.10m \)) and time-averaged from 4.0 seconds
to 5.5 seconds after the statistically steady state is reached. It can be seen that
a dense region (with solids voidage of about 0.1) is present up until about 0.25 m
from the bottom. Further upward, the solids voidage decreases exponentially. The
concentration of gas species and fine PM number density decrease rapidly close to
the bottom due to high sorbent concentrations, but levels off toward the top. About
32% of fine PM is captured onto sorbent particles, 65% of \( SO_2 \) has been chemically
adsorbed onto lime, and 74% of mercury has been physically adsorbed onto activated
carbon. At the statistically-stationary state, the carbon-to-mercury (\( C : Hg \)) mass
ratio is about 13,000 for these conditions, based on a flow rate of activated carbon of
about \( 4 \times 10^{-6} \text{kg/s} \). In their bench-scale experiments of direct injection of activated
carbon into a flue-gas stream, Serre et al. [73] obtained mercury removal efficiencies
of 50% or greater for \( C : Hg \) ratios in this range, depending on the type of activated
carbon. Figure 4.22 indicates about 76% of incoming elemental mercury is captured
before secondary injection of activated carbon occurs at 5.5 seconds.

To capture more mercury vapor or all mercury vapor, more activated carbon is
injected from both sides after 5.5 seconds of operation with a flow rate of 0.02475 kg/s, where $\alpha_s = 0.5$, $Y_{s1} = 1 - Y_{s2} = 0$, $u_s = \pm 0.0165 m/s$ (both sides) ($0.04 \times 0.05$ m in width and height, $z=0.5$) from 5.5 seconds to 6.5 seconds. So in total, 0.0495 kg of activated carbon is injected to the CFBA in order to capture more mercury vapor.

Figures 4.23-4.25 show snapshots of fine PM number density, $SO_2$ and $Hg$ mass concentration distribution, respectively. It can be seen that fine PM normalized number density decreases greatly until about 0.25 m from the bottom during the statistically steady state after 5.5 seconds of operation due to dense sorbent particles close to the bottom, which can be seen in the snapshot of solids mixture volume fraction in Figure 4.26. $SO_2$ concentration evolution is similar to that of fine PM, but it can be seen that the concentration of $SO_2$ increases a little after 12 of seconds of operation. This is due to the decrease in available $CaO$ over time due to chemical adsorption. After secondary activated carbon injection, almost all mercury vapor disappears above 0.25 m from the bottom by 12 seconds.

Figure 4.26 and Figure 4.27 show snapshots of solids mixture voidage fraction and activated carbon voidage fraction, respectively. Three locations with high light in Figure 4.27 are side inlet at the bottom and activated carbon injection on both sides. It can be found that the activated carbon accumulates close to the wall at 6.5 seconds. It takes about 1.0 seconds for the activated carbon to disperse inside the dense region close to the bottom. The newly injected activated carbon can be regarded as being well-mixed within the reactor by 9.3 seconds.

Figure 4.28 shows mixture solids mass flux versus physical time. The occurrence of a statistically steady state after about 4 seconds can be seen, and the average mass flux is about $0.1 kg/m^2s$. Figures 4.29-4.31 show the time-resolved mass flow rates at the top and bottom of the riser for fine PM, $SO_2$ and $Hg$, respectively. The statistically steady states can also be seen from these three figures. It can be found
Figure 4.23: A snapshot for fine PM
Figure 4.24: A snapshot for $SO_2$
Figure 4.25: A snapshot for Hg
Figure 4.26: A snapshot for solids mixture volume fraction
Figure 4.27: A snapshot for activated carbon volume fraction
that the mass flow rate for $SO_2$ at the top of CFBA increases after 4.0 seconds. This is due to less and less $CaO$ left inside the riser as chemical adsorption progresses. For example, $X_{CaO}$ is 0.01 at the beginning and 0.00079 after 5.5 seconds of operation. It can be expected to decrease continuously with the chemical adsorption evolution, until finally all $CaO$ will be used up and the mass flow rate of $SO_2$ at the top will be the same as that at the bottom.

It is interesting to note in Figure 4.31 that mercury vapor mass flow rate does not decrease immediately after activated carbon is injected after 5.5 seconds. There are two reasons for this phenomenon: firstly, there is a duration or residence time required to let mercury vapor above 0.5 m height to exit the riser; secondly, most of the injected activated carbon accumulates close to the wall initially, which can be seen in Figure 4.25. Thus there is no good contact between mercury vapor and the newly-injected activated carbon inside the riser except close to the wall. Only after activated carbon totally disperses within the bottom of riser, which takes about 1.0 seconds after injection, can the injected activated carbon physically adsorb as much mercury vapor as the old activated carbon does inside the riser from the beginning. Here, the physical adsorption rate is regarded as constant with the initial adsorption rate as developed in Section 2.5.3, and the effects of catalyst saturation are thus not accounted for.

Figure 4.32 shows the planar-averaged and time-averaged fine PM, $SO_2$ and $Hg$ concentration between 10 seconds and 12 seconds during the statistically steady state. Almost all mercury vapor has been adsorbed onto activated carbon. Most of the activated carbon stays close to the bottom, so the mercury vapor mass fraction decreases greatly up until about 0.25 m from the bottom.
Figure 4.28: Solids mixture mass flux at the top versus physical time

Figure 4.29: Fine PM normalized number density flow rate at the top of the CFBA
Figure 4.30: $SO_2$ mass flow rate at the top of the CFBA

Figure 4.31: $Hg$ mass flow rate at the top of the CFBA
Figure 4.32: Averaged species concentration inside the CFBA

5 Conclusions and Future Work

5.1 Conclusion

The utilization of coal for energy production poses considerable environmental concerns in that it results in emissions of harmful pollutants such as $SO_2$, $NO_x$, fine particulate matter, and trace heavy metals such as mercury. Circulating fluidized bed adsorbers are being considered as a stop-gap technology that may enable existing coal-fired power plants to meet new emissions regulations with less expense. This work has centered around developing a computational fluid dynamics-based approach for analyzing CFBA configurations for multi-pollutant control.

In order to simulate such a complex two-phase flow, we have developed modeling and simulation strategies for CFBAs and similar gas-solid flows. This framework includes the use of low-diffusion flux-splitting methods for solving the gas mixture/solids mixture system, the inclusion of sub-models for fine particulate matter agglomeration
onto sorbent particles, $SO_2$ chemical adsorption and $Hg$ physical adsorption, and the development of methods for extracting particle residence time distributions from a particle mixing model.

Each component of the framework has been independently tested in detail through trade-off studies, benchmark flow calculations, and comparison with experimental data. The complete framework has been applied to simulate simultaneous $SO_2$, mercury, and fine PM capture within a laboratory-scale circulating fluidized bed reactor. Though no comparisons with experimental data have yet been made, the predictions with regard to pollutant capture efficiency are plausible.

5.2 Future work

Future work will be concentrated on further validation of the three-dimensional model for realistic gas-solid reactors and its use in analyzing the performance of such reactors. One process of interest is the combination of activated carbon injection with semi-dry flue gas desulfurization technology as a means of simultaneously removing elementary mercury and $SO_2$ at relatively low temperatures. This work will require the extension of the mercury adsorption model to include the effects of long-time catalyst saturation, lime injection as part of a slurry with liquid water, and heat loss due to liquid water evaporation.
References


Appendix

A  Jacobian Matrices

\[ P \frac{\partial V}{\partial W} = \frac{1}{J} \begin{bmatrix} \left[ P \frac{\partial V}{\partial W} \right]_{\text{gas}} & 0 \\ 0 & \left[ P \frac{\partial V}{\partial W} \right]_{\text{solids}} \end{bmatrix} \]  \hspace{1cm} (a-1)

\[ M \frac{\partial V}{\partial W} = \frac{1}{J} \begin{bmatrix} M_{g3} & M_{g4} & 0 & M_{s4,g} \\ 0 & 0 & M_{s2} & M_{s4,s} \end{bmatrix} \]  \hspace{1cm} (a-2)
\[
\left[ \frac{P}{\partial V} \right]_{\text{gas}} = \frac{1}{J} \begin{bmatrix}
Y_{g1} & Y_{g2} & Y_{g3} & p_g & u_g & v_g & w_g \\
0 & 0 & 0 & \frac{Y_{g1}}{\beta_g^2} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{Y_{g2}}{\beta_g^2} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{Y_{g3}}{\beta_g^2} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{1}{\beta_g^2} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{u_g}{\beta_g^2} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{v_g}{\beta_g^2} & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{w_g}{\beta_g^2} & 0 & 0 & 0 \\
\end{bmatrix}
\] (a-3)

\[
\left[ \frac{P}{\partial V} \right]_{\text{solids}} = \frac{1}{J} \begin{bmatrix}
X_{\text{CaO}} & Y_{s1} & \alpha_s & u_s & v_s & w_s \\
0 & 0 & \rho_s \frac{a_s^2 Y_{s1} X_{\text{CaO}}}{\beta_s^2} & 0 & 0 & 0 \\
0 & 0 & \rho_s \frac{a_s^2 Y_{s1}}{\beta_s^2} & 0 & 0 & 0 \\
0 & 0 & \rho_s \frac{a_s^2 \alpha_s}{\beta_s^2} & 0 & 0 & 0 \\
0 & 0 & \rho_s \frac{a_s^2 v_s}{\beta_s^2} & 0 & 0 & 0 \\
0 & 0 & \rho_s \frac{a_s^2 w_s}{\beta_s^2} & 0 & 0 & 0 \\
0 & 0 & \rho_s \frac{a_s^2 u_s}{\beta_s^2} & 0 & 0 & 0 \\
\end{bmatrix}
\] (a-4)
\[ M_{g3} = \frac{1}{J} \begin{bmatrix} Y_{g1} & Y_{g2} & -\rho_{g} \alpha_{g} Y_{g1} - \rho_{H_{g,g}} \alpha_{g} Y_{g1} \\ \rho_{g} \alpha_{g} & 0 & -\rho_{g} \alpha_{g} Y_{g2} + \rho_{g} \alpha_{g} Y_{g2} \\ 0 & -\rho_{g} \alpha_{g} Y_{g3} - \rho_{H_{g,g}} \alpha_{g} Y_{g3} + \rho_{g} \alpha_{g} Y_{g3} \\ 0 & 0 & -\rho_{H_{g,g}} \alpha_{g} \\ 0 & 0 & -\rho_{H_{g,g}} \alpha_{g} \\ 0 & 0 & -\rho_{H_{g,g}} \alpha_{g} \\ 0 & 0 & -\rho_{H_{g,g}} \alpha_{g} \\ 0 & 0 & -\rho_{g} \alpha_{g} u_{g} \\ 0 & 0 & -\rho_{g} \alpha_{g} v_{g} \\ 0 & 0 & -\rho_{g} \alpha_{g} w_{g} \end{bmatrix} \] (a-5)

\[ M_{g4} = \frac{1}{J} \begin{bmatrix} p_{g} & u_{g} & v_{g} & w_{g} \\ \frac{1}{a_{g}^2} \alpha_{g} Y_{g1} & 0 & 0 & 0 \\ \frac{1}{a_{g}^2} \alpha_{g} Y_{g2} & 0 & 0 & 0 \\ \frac{1}{a_{g}^2} \alpha_{g} Y_{g3} & 0 & 0 & 0 \\ \frac{1}{a_{g}^2} \alpha_{g} & 0 & 0 & 0 \\ \frac{1}{a_{g}^2} \alpha_{g} u_{g} & \rho_{g} & 0 & 0 \\ \frac{1}{a_{g}^2} \alpha_{g} v_{g} & 0 & \rho_{g} & 0 \\ \frac{1}{a_{g}^2} \alpha_{g} w_{g} & 0 & 0 & \rho_{g} \end{bmatrix} \] (a-6)
where, $X_m$ is the reciprocal of molecular weight, and $M_{Inert}$ is the average molecular weight for the inertia gases or other gases.

$$X_m = \left( \frac{Y_{SO_2}}{M_{SO_2}} + \frac{Y_{Hg}}{M_{Hg}} + \frac{Y_{O_2}}{M_{O_2}} + \frac{Y_{SO_2} - Y_{Hg} - Y_{O_2}}{M_{Inert}} \right)$$

$$\rho_{SO_2,g} = \frac{\rho_g}{X_m} \left( \frac{1}{M_{SO_2}} - \frac{1}{M_{Inert}} \right) \quad (a-7)$$

$$\rho_{Hg,g} = \frac{\rho_g}{X_m} \left( \frac{1}{M_{Hg}} - \frac{1}{M_{Inert}} \right)$$

$$\frac{1}{M_{Inert}} = \frac{1}{Y_{N2}+Y_{CO_2}+Y_{H2O}} \left[ \frac{Y_{N2}}{M_{N2}} + \frac{Y_{CO_2}}{M_{CO_2}} + \frac{Y_{H2O}}{M_{H2O}} \right]$$

$M_{s2} = \frac{1}{J}$

$$\begin{bmatrix}
    X_{CaO} & Y_{s1} \\
    \alpha_s Y_{s1} \left( \frac{\partial \rho_g}{\partial X_{CaO}} X_{CaO} + \rho_s \right) & \alpha_s X_{CaO} \left( \frac{\partial \rho_g}{\partial Y_{s1}} Y_{s1} + \rho_s \right) \\
    \alpha_s Y_{s1} \frac{\partial \rho_s}{\partial X_{CaO}} & \alpha_s \left( \frac{\partial \rho_s}{\partial Y_{s1}} Y_{s1} + \rho_s \right) \\
    \alpha_s \frac{\partial \rho_s}{\partial X_{CaO}} & \alpha_s \frac{\partial \rho_s}{\partial Y_{s1}} \\
    \alpha_s \frac{\partial \rho_s}{\partial X_{CaO}} & \alpha_s \frac{\partial \rho_s}{\partial Y_{s1}} \\
    \alpha_s \frac{\partial \rho_s}{\partial X_{CaO}} & \alpha_s \frac{\partial \rho_s}{\partial Y_{s1}} \\
    \alpha_s \frac{\partial \rho_s}{\partial X_{CaO}} & \alpha_s \frac{\partial \rho_s}{\partial Y_{s1}}
\end{bmatrix} \quad (a-8)$$
\[
M_{s4,g} = \frac{1}{J} \begin{bmatrix}
\alpha_s & u_s & v_s & w_s \\
-\rho g Y_{g1} & 0 & 0 & 0 \\
-\rho g Y_{g2} & 0 & 0 & 0 \\
-\rho g Y_{g3} & 0 & 0 & 0 \\
\rho g & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{bmatrix}
\]

(a-9)

\[
M_{s4,s} = \frac{1}{J} \begin{bmatrix}
\alpha_s & u_s & v_s & w_s \\
\rho_s Y_{s1} X_{CaO} & 0 & 0 & 0 \\
\rho_s Y_{s1} & 0 & 0 & 0 \\
\rho_s & 0 & 0 & 0 \\
0 & \rho_s & 0 & 0 \\
0 & 0 & \rho_s & 0 \\
0 & 0 & 0 & \rho_s
\end{bmatrix}
\]

(a-10)

\[
(P + M) \frac{\partial V}{\partial W} = \frac{1}{J} \begin{bmatrix}
(P + M)_{g3} & (P + M)_{g4} & 0 & (P + M)_{s4,g} \\
0 & 0 & (P + M)_{s2} & (P + M)_{s4,s}
\end{bmatrix}
\]

(a-11)
\[(P + M)_{g3} = \frac{1}{J} \begin{bmatrix}
Y_{g1} & Y_{g2} & Y_{g3} \\
\rho_g\alpha_g & -\rho_{so2,g}\alpha_g Y_{g1} & -\rho_{Hg,g}\alpha_g Y_{g1} \\
0 & -\rho_{so2,g}\alpha_g Y_{g2} + \rho_g\alpha_g & -\rho_{Hg,g}\alpha_g Y_{g2} \\
0 & -\rho_{so2,g}\alpha_g Y_{g3} & -\rho_{Hg,g}\alpha_g Y_{g3} + \rho_g\alpha_g \\
0 & -\rho_{so2,g}\alpha_g u_g & -\rho_{Hg,g}\alpha_g u_g \\
0 & -\rho_{so2,g}\alpha_g v_g & -\rho_{Hg,g}\alpha_g v_g \\
0 & -\rho_{so2,g}\alpha_g w_g & -\rho_{Hg,g}\alpha_g w_g 
\end{bmatrix} \quad (a-12)\]

\[(P + M)_{g4} = \frac{1}{J} \begin{bmatrix}
P_g & u_g & v_g & w_g \\
\frac{1}{\alpha_g^2}\alpha_g Y_{g1} + \frac{Y_{g1}}{\beta_g^2} & 0 & 0 & 0 \\
\frac{1}{\alpha_g^2}\alpha_g Y_{g2} + \frac{Y_{g2}}{\beta_g^2} & 0 & 0 & 0 \\
\frac{1}{\alpha_g^2}\alpha_g Y_{g3} + \frac{Y_{g3}}{\beta_g^2} & 0 & 0 & 0 \\
\frac{1}{\alpha_g^2}\alpha_g + \frac{1}{\beta_g^2} & 0 & 0 & 0 \\
\frac{1}{\alpha_g^2}\alpha_g u_g + \frac{u_g}{\beta_g^2} & \rho_g & 0 & 0 \\
\frac{1}{\alpha_g^2}\alpha_g v_g + \frac{v_g}{\beta_g^2} & 0 & \rho_g & 0 \\
\frac{1}{\alpha_g^2}\alpha_g w_g + \frac{w_g}{\beta_g^2} & 0 & 0 & \rho_g 
\end{bmatrix} \quad (a-13)\]
\[(P + M)_{s2} = \frac{1}{J}\]

\[
\begin{bmatrix}
X_{\text{CaO}} & Y_{s1} \\
\alpha_s Y_{s1} \left( \frac{\partial \rho_s}{\partial X_{\text{CaO}}} X_{\text{CaO}} + \rho_s \right) & \alpha_s X_{\text{CaO}} \left( \frac{\partial \rho_s}{\partial Y_{s1}} Y_{s1} + \rho_s \right) \\
\alpha_s Y_{s1} \frac{\partial \rho_s}{\partial X_{\text{CaO}}} & \alpha_s \left( \frac{\partial \rho_s}{\partial Y_{s1}} Y_{s1} + \rho_s \right) \\
\alpha_s u_s \frac{\partial \rho_s}{\partial X_{\text{CaO}}} & \alpha_s u_s \frac{\partial \rho_s}{\partial Y_{s1}} \\
\alpha_s v_s \frac{\partial \rho_s}{\partial X_{\text{CaO}}} & \alpha_s v_s \frac{\partial \rho_s}{\partial Y_{s1}} \\
\alpha_s w_s \frac{\partial \rho_s}{\partial X_{\text{CaO}}} & \alpha_s w_s \frac{\partial \rho_s}{\partial Y_{s1}}
\end{bmatrix}
\]

\[(a-14)\]

\[(P + M)_{s4,g} = \frac{1}{J}\]

\[
\begin{bmatrix}
\alpha_s & u_s & v_s & w_s \\
-\rho_g Y_{g1} & 0 & 0 & 0 \\
-\rho_g Y_{g2} & 0 & 0 & 0 \\
-\rho_g Y_{g3} & 0 & 0 & 0 \\
-\rho_g & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0
\end{bmatrix}
\]

\[(a-15)\]
\[ (P + M)_{s4,s} = \frac{1}{J} \begin{bmatrix}
\alpha_s & u_s & v_s & w_s \\
\rho_s Y_{s1} X_{CaO} + \rho_s \frac{a_s^2 Y_{s1} X_{CaO}}{\beta_s^2} & 0 & 0 & 0 \\
\rho_s Y_{s1} + \rho_s \frac{a_s^2 Y_{s1}}{\beta_s^2} & 0 & 0 & 0 \\
\rho_s + \rho_s \frac{\alpha_s^2}{\beta_s^2} & 0 & 0 & 0 \\
\rho_s u_s \frac{\alpha_s^2}{\beta_s^2} & \rho_s & 0 & 0 \\
\rho_s v_s \frac{\alpha_s^2}{\beta_s^2} & 0 & \rho_s & 0 \\
\rho_s w_s \frac{\alpha_s^2}{\beta_s^2} & 0 & 0 & \rho_s
\end{bmatrix} \]  

(a-16)

Jacobian Matrix for convection terms

\[
\frac{\partial F_k}{\partial V} \frac{\partial V}{\partial W} = \frac{1}{J} \begin{bmatrix} J_g \\ J_s \end{bmatrix}
\]

\[
J_g = \begin{bmatrix} J_{g,3} & J_{g,4} & J_{g,s} \\ 0 & J_{s,2} & J_{s,4} \end{bmatrix}
\]

\[
J_{g,3} = \begin{bmatrix} y_1 & y_2 & y_3 \\ \rho_g \alpha_g U_{g,k} & -\rho_{so2,g} \alpha_g U_{g,k} Y_{g1} & -\rho_{hg,g} \alpha_g U_{g,k} Y_{g1} \\ 0 & \rho_g \alpha_g U_{g,k} - \rho_{so2,g} \alpha_g U_{g,k} Y_{g2} & -\rho_{hg,g} \alpha_g U_{g,k} Y_{g2} \\ 0 & -\rho_{so2,g} \alpha_g U_{g,k} Y_{g3} & \rho_g \alpha_g U_{g,k} - \rho_{hg,g} \alpha_g U_{g,k} Y_{g3} \\ 0 & -\rho_{so2,g} \alpha_g U_{g,k} u_g & -\rho_{hg,g} \alpha_g U_{g,k} u_g \\ 0 & -\rho_{so2,g} \alpha_g U_{g,k} v_g & -\rho_{hg,g} \alpha_g U_{g,k} v_g \\ 0 & -\rho_{so2,g} \alpha_g U_{g,k} w_g & -\rho_{hg,g} \alpha_g U_{g,k} w_g \end{bmatrix}
\]

(a-18)
\[ \mathbf{J}_{g,4} = \begin{bmatrix} \mathbf{P}_g & \mathbf{u}_g & \mathbf{v}_g & \mathbf{w}_g \end{bmatrix} \]

\[
\begin{align*}
\frac{\alpha_g U_{g,k} Y_1}{a_g^2} & \quad \rho_g c^k Y_1 & \quad \rho_g c^k Y_1 & \quad \rho_g c^k Y_1 \\
\frac{\alpha_g U_{g,k} Y_2}{a_g^2} & \quad \rho_g c^k Y_2 & \quad \rho_g c^k Y_2 & \quad \rho_g c^k Y_2 \\
\frac{\alpha_g U_{g,k} Y_3}{a_g^2} & \quad \rho_g c^k Y_3 & \quad \rho_g c^k Y_3 & \quad \rho_g c^k Y_3 \\
\frac{\alpha_g U_{g,k} u_g}{a_g^2} & \quad \rho_g c^k u_g + \rho_g U_{g,k} & \quad \rho_g c^k u_g & \quad \rho_g c^k u_g \\
\frac{\alpha_g U_{g,k} v_g}{a_g^2} & \quad \rho_g c^k v_g & \quad \rho_g c^k v_g + \rho_g U_{g,k} & \quad \rho_g c^k v_g \\
\frac{\alpha_g U_{g,k} w_g}{a_g^2} & \quad \rho_g c^k w_g & \quad \rho_g c^k w_g & \quad \rho_g c^k w_g + \rho_g U_{g,k} 
\end{align*}
\]

\[ \mathbf{J}_{g,s} = \begin{bmatrix} x_{CaO} & Y_{s1} & \alpha_s & u_s & v_s & w_s \end{bmatrix} \]

\[
\begin{align*}
&0 & 0 & 0 & 0 & 0 & 0 \\
&0 & 0 & 0 & 0 & 0 & 0 \\
&0 & 0 & 0 & 0 & 0 & 0 \\
&0 & 0 & 0 & 0 & 0 & 0 \\
&\rho_g U_{g,k} u_g & 0 & 0 & 0 \\
&\rho_g U_{g,k} v_g & 0 & 0 & 0 \\
&\rho_g U_{g,k} w_g & 0 & 0 & 0 
\end{align*}
\]
\[
\begin{align*}
\mathbf{J}_{s,2} &= \\
\begin{bmatrix}
\frac{\partial \rho_s}{\partial X_{CaO}} \alpha_s U_{s,k} Y_{s1} X_{CaO} + \rho_s \alpha_s U_{s,k} Y_{s1} & \frac{\partial \rho_s}{\partial Y_{s1}} \alpha_s U_{s,k} Y_{s1} + \rho_s \alpha_s U_{s,k} \\
\frac{\partial \rho_s}{\partial X_{CaO}} \alpha_s U_{s,k} Y_{s1} & \frac{\partial \rho_s}{\partial Y_{s1}} \alpha_s U_{s,k} Y_{s1} + \rho_s \alpha_s U_{s,k} \\
\frac{\partial \rho_s}{\partial X_{CaO}} \alpha_s U_{s,k} u_s + \xi_k \frac{\partial \rho_s}{\partial \rho_s} \frac{\partial \rho_s}{\partial X_{CaO}} & \frac{\partial \rho_s}{\partial Y_{s1}} \alpha_s U_{s,k} u_s + \xi_k \frac{\partial \rho_s}{\partial \rho_s} \frac{\partial \rho_s}{\partial Y_{s1}} \\
\frac{\partial \rho_s}{\partial X_{CaO}} \alpha_s U_{s,k} v_s + \xi_k \frac{\partial \rho_s}{\partial \rho_s} \frac{\partial \rho_s}{\partial X_{CaO}} & \frac{\partial \rho_s}{\partial Y_{s1}} \alpha_s U_{s,k} v_s + \xi_k \frac{\partial \rho_s}{\partial \rho_s} \frac{\partial \rho_s}{\partial Y_{s1}} \\
\frac{\partial \rho_s}{\partial X_{CaO}} \alpha_s U_{s,k} w_s + \xi_k \frac{\partial \rho_s}{\partial \rho_s} \frac{\partial \rho_s}{\partial X_{CaO}} & \frac{\partial \rho_s}{\partial Y_{s1}} \alpha_s U_{s,k} w_s + \xi_k \frac{\partial \rho_s}{\partial \rho_s} \frac{\partial \rho_s}{\partial Y_{s1}}
\end{bmatrix}
\end{align*}
\]

\[
\frac{1}{\rho_s} = y_{s1} \left( \frac{X_{CaO}}{\rho_{CaO}} + \frac{1 - X_{CaO}}{\rho_{CaSO4}} \right) + \frac{1 - y_{s1}}{\rho_{s2}}
\]

\[
\frac{\partial \rho_s}{\partial X_{CaO}} = -y_{s1} \rho_s^2 \left[ \left( \frac{1}{\rho_{CaO}} - \frac{1}{\rho_{CaSO4}} \right) \right]
\]

\[
\frac{\partial \rho_s}{\partial Y_{s1}} = -\rho_s^2 \left[ \left( \frac{X_{CaO}}{\rho_{CaO}} + \frac{1 - X_{CaO}}{\rho_{CaSO4}} \right) - \frac{1}{\rho_{s2}} \right]
\]

\[
\frac{\partial \rho_s}{\partial \rho_s} = C_s \left[ \alpha_s + 2 \alpha_{s,\text{max}} \ln(1 - \frac{\alpha_s}{\alpha_{s,\text{max}}}) - \frac{\alpha_s \alpha_{s,\text{max}}}{\alpha_s - \alpha_{s,\text{max}}} \right] = \frac{p_s}{\rho_s}
\]

\[
\mathbf{J}_{s,4} = \\
\begin{bmatrix}
0 & \rho_s \xi_{s2} Y_{s1} X_{CaO} & \rho_s \xi_{s2} Y_{s1} X_{CaO} & \rho_s \xi_{s2} Y_{s1} X_{CaO} \\
0 & \rho_s \xi_{s2} Y_{s1} & \rho_s \xi_{s2} Y_{s1} & \rho_s \xi_{s2} Y_{s1} \\
0 & \rho_s \xi_k & \rho_s \xi_k & \rho_s \xi_k \\
-\rho_s U_{s,k} u_s + \xi_k \rho_s a_s^2 & \rho_s \xi_k u_s + \rho_s U_{s,k} & \rho_s \xi_k u_s & \rho_s \xi_k u_s \\
-\rho_s U_{s,k} v_s + \xi_k \rho_s a_s^2 & \rho_s \xi_k v_s & \rho_s \xi_k v_s + \rho_s U_{s,k} & \rho_s \xi_k v_s \\
-\rho_s U_{s,k} w_s + \xi_k \rho_s a_s^2 & \rho_s \xi_k w_s & \rho_s \xi_k w_s & \rho_s \xi_k w_s + \rho_s U_{s,k}
\end{bmatrix}
\]
Jacobian Matrix for source terms

\[ \frac{\partial S}{\partial W} = \begin{bmatrix} S_{g3} & S_{g4} & S_{s6} \end{bmatrix} \]  \hspace{1cm} (a-24)

\[ S_{W,g3} = \begin{bmatrix}
Y_{g1} & Y_{g2} & Y_{g3} \\
\frac{\partial s_{g1}}{\partial Y_{g1}} & \frac{\partial s_{g1}}{\partial Y_{g2}} & \frac{\partial s_{g1}}{\partial Y_{g3}} \\
0 & \frac{\partial s_{g2}}{\partial Y_{g2}} & \frac{\partial s_{g2}}{\partial Y_{g3}} \\
0 & \frac{\partial s_{g3}}{\partial Y_{g2}} & \frac{\partial s_{g3}}{\partial Y_{g3}} \\
0 & \frac{\partial s_{g4}}{\partial Y_{g2}} & \frac{\partial s_{g4}}{\partial Y_{g3}} \\
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
\end{bmatrix}

\[ \frac{\partial s_{g1}}{\partial Y_{g1}} = -k_a \alpha_a \rho_g \alpha_g \]  \hspace{1cm} (a-26)
\[
\frac{\partial s_{g1}}{\partial y_{g2}} = \kappa_s \alpha_s \frac{1}{x_m} \left( \frac{1}{M_{SO2}} - \frac{1}{M_{Inert}} \right) \rho_g \alpha_g Y_{g1}
\]
\[
\frac{\partial s_{g2}}{\partial y_{g2}} = C_{s,g2} R_{g2}
\]
\[
\frac{\partial s_{g3}}{\partial y_{g2}} = -C_{s,g3} \rho_s \alpha_s Y_{g2} C_{eff}^{C1} \left[ \rho_g \alpha_g Y_{g3} \right]^{C_{eff}^{C1} - 1} \frac{1}{x_m} \left( \frac{1}{M_{SO2}} - \frac{1}{M_{Inert}} \right) \rho_g \alpha_g Y_{g3}
\]
\[
\frac{\partial s_{g4}}{\partial y_{g2}} = \left( 1 + \frac{M_{O2}}{M_{SO2}} \right) \frac{\partial s_{g2}}{\partial y_{g2}} + \frac{\partial s_{g3}}{\partial y_{g2}}
\]
\[
\frac{\partial s_{Xcao}}{\partial y_{g2}} = C_{s,1} R_{g2}
\]
\[
\frac{\partial s_{Y_{s1}}}{\partial y_{g2}} = \left( 1 - \frac{M_{CaSO4}}{M_{CaO}} \right) \frac{\partial s_{Xcao}}{\partial y_{g2}}
\]
\[
\frac{\partial s_{Y_{s2}}}{\partial y_{g2}} = \frac{\partial s_{Y_{s1}}}{\partial y_{g2}} - \frac{\partial s_{Y_{s3}}}{\partial y_{g2}}
\]
\[
R_{g2} = -\rho_s \alpha_s Y_{s1} X_{CaO} \frac{1}{x_m} \left( \frac{1}{M_{SO2}} - \frac{1}{M_{Inert}} \right) \rho_g \alpha_g Y_{g2} + \rho_s \alpha_s Y_{s1} X_{CaO} \rho_g \alpha_g
\]
\[
\frac{\partial s_{g1}}{\partial y_{g3}} = \kappa_s \alpha_s \frac{1}{M_{Hg}} \left( \frac{1}{M_{Hg}} - \frac{1}{M_{Inert}} \right) \rho_g \alpha_g Y_{g1}
\]
\[
\frac{\partial s_{g2}}{\partial y_{g3}} = C_{s,g2} R_{g3}
\]
\[
\frac{\partial s_{g3}}{\partial y_{g3}} = -C_{s,g3} \rho_s \alpha_s Y_{g2} C_{eff}^{C1} \left[ \rho_g \alpha_g Y_{g3} \right]^{C_{eff}^{C1} - 1} \frac{1}{X_m} \left( \frac{1}{M_{Hg}} - \frac{1}{M_{Inert}} \right) - \rho_g \alpha_g
\]
\[
\frac{\partial s_{g4}}{\partial y_{g3}} = \left( 1 + \frac{M_{O2}}{M_{SO2}} \right) \frac{\partial s_{g2}}{\partial y_{g3}} + \frac{\partial s_{g3}}{\partial y_{g3}}
\]
\[
\frac{\partial s_{Xcao}}{\partial y_{g3}} = C_{s,1} R_{g3}
\]
\[
\frac{\partial s_{Y_{s1}}}{\partial y_{g3}} = \left( 1 - \frac{M_{CaSO4}}{M_{CaO}} \right) \frac{\partial s_{Xcao}}{\partial y_{g3}}
\]
\[
\frac{\partial s_{Y_{s2}}}{\partial y_{g3}} = \frac{\partial s_{Y_{s1}}}{\partial y_{g3}} - \frac{\partial s_{Y_{s3}}}{\partial y_{g3}}
\]
\[
R_{g3} = -C_{s,g2} \rho_s \alpha_s Y_{s1} X_{CaO} \frac{1}{x_m} \left( \frac{1}{M_{Hg}} - \frac{1}{M_{Inert}} \right) \rho_g \alpha_g Y_{g2}
\]
\[
S_{W,g4} = \begin{bmatrix}
  p_g & u_g & v_g & w_g \\
  \frac{\partial s_{g1}}{\partial p_g} & 0 & 0 & 0 \\
  \frac{\partial s_{g2}}{\partial p_g} & 0 & 0 & 0 \\
  \frac{\partial s_{g3}}{\partial p_g} & 0 & 0 & 0 \\
  \frac{\partial s_{g4}}{\partial p_g} & 0 & 0 & 0 \\
  0 & -\frac{\beta}{\alpha_g} & 0 & 0 \\
  0 & 0 & -\frac{\beta}{\alpha_g} & 0 \\
  -\frac{g}{\alpha_g^2} & 0 & 0 & -\frac{\beta}{\alpha_g} \\
  \alpha_g \frac{g}{\alpha_g ^2} & 0 & 0 & \frac{\beta}{\alpha_g} \\
\end{bmatrix}
\] (a-29)

\[
\frac{\partial s_{g1}}{\partial p_g} = -\kappa_s \alpha_s \frac{1}{\alpha_g^2} \alpha_g Y_{g1}
\]

\[
\frac{\partial s_{g2}}{\partial p_g} = C_{s,g2} \rho_s \alpha_s Y_{s1} X_{CaO} \frac{1}{\alpha_g^2} \alpha_g Y_{g2}
\]

\[
\frac{\partial s_{g3}}{\partial p_g} = C_{s,g3} \rho_s \alpha_s Y_{s2} C_{eff}^1 \left[ \rho_s \alpha_g Y_{g3} \right] C_{eff}^{-1} \frac{1}{\alpha_g^2} \alpha_g Y_{g3}
\]

\[
\frac{\partial s_{g4}}{\partial p_g} = \frac{\partial s_{g3}}{\partial p_g} + \left( 1 + \frac{M_{CaS}}{M_{SO2}} \right) \frac{\partial s_{g2}}{\partial p_g}
\] (a-30)

\[
\frac{\partial s_{X_{calc}}}{\partial Y_{g2}} = C_{s1} \rho_s \alpha_s Y_{s1} X_{CaO} \frac{1}{\alpha_g} \alpha_g Y_{g2}
\]

\[
\frac{\partial Y_{s1}}{\partial p_g} = \left( 1 - \frac{M_{CaSO4}}{M_{CaO}} \right) \frac{\partial s_{X_{calc}}}{\partial p_g}
\]

\[
\frac{\partial Y_{s2}}{\partial p_g} = \frac{\partial Y_{s1}}{\partial p_g} - \frac{\partial Y_{s2}}{\partial p_g}
\]
\[ S_{Ws6} = \begin{bmatrix}
X_{cao} & Y_{s1} & \alpha_s & u_s & v_s & w_s \\
0 & 0 & \frac{\partial s_{s2}}{\partial \alpha_s} & 0 & 0 & 0 \\
\frac{\partial s_{s2}}{\partial X_{cao}} & \frac{\partial s_{s2}}{\partial Y_{s1}} & \frac{\partial s_{s2}}{\partial \alpha_s} & 0 & 0 & 0 \\
\frac{\partial s_{s3}}{\partial X_{cao}} & \frac{\partial s_{s3}}{\partial Y_{s1}} & \frac{\partial s_{s3}}{\partial \alpha_s} & 0 & 0 & 0 \\
\frac{\partial s_{s4}}{\partial X_{cao}} & \frac{\partial s_{s4}}{\partial Y_{s1}} & \frac{\partial s_{s4}}{\partial \alpha_s} & 0 & 0 & 0 \\
0 & 0 & -\beta \left[ \frac{u_s}{\alpha_s} + \frac{u_s}{\alpha_s} \right] & \frac{\beta}{\alpha_s} & 0 & 0 \\
0 & 0 & -\beta \left[ \frac{v_s}{\alpha_s} + \frac{v_s}{\alpha_s} \right] & 0 & \frac{\beta}{\alpha_s} & 0 \\
0 & 0 & -\beta \left[ \frac{w_s}{\alpha_s} + \frac{w_s}{\alpha_s} \right] & 0 & 0 & \frac{\beta}{\alpha_s} \\
\frac{\partial s_{X_{cao}}}{\partial X_{cao}} & \frac{\partial s_{Y_{s1}}}{\partial X_{cao}} & \frac{\partial s_{Y_{s1}}}{\partial \alpha_s} & 0 & 0 & 0 \\
\frac{\partial s_{Y_{s1}}}{\partial X_{cao}} & \frac{\partial s_{Y_{s1}}}{\partial Y_{s1}} & \frac{\partial s_{Y_{s1}}}{\partial \alpha_s} & 0 & 0 & 0 \\
\frac{\partial s_{s4}}{\partial X_{cao}} & \frac{\partial s_{s4}}{\partial Y_{s1}} & \frac{\partial s_{s4}}{\partial \alpha_s} & 0 & 0 & 0 \\
0 & 0 & \beta \left[ \frac{u_s}{\alpha_s} + \frac{u_s}{\alpha_s} \right] & -\frac{\beta}{\alpha_s} & 0 & 0 \\
0 & 0 & \beta \left[ \frac{v_s}{\alpha_s} + \frac{v_s}{\alpha_s} \right] & 0 & -\frac{\beta}{\alpha_s} & 0 \\
0 & 0 & \beta \left[ \frac{w_s}{\alpha_s} + \frac{w_s}{\alpha_s} \right] - (\rho_s - \rho_g) g & 0 & 0 & -\frac{\beta}{\alpha_s} \\
\end{bmatrix} \quad (a-31) \]
\[
\begin{align*}
\frac{\partial s_{g2}}{\partial X_{cao}} &= C_{s,g2} \frac{\partial \rho_s}{\partial X_{cao}} \alpha_s Y_{s1} X_{CaO \rho_g \alpha_g Y_{g2}} + C_{s,g2} \rho_s \alpha_s Y_{s1} \rho_g \alpha_g Y_{g2} \\
\frac{\partial s_{g3}}{\partial X_{cao}} &= C_{s,g3} \frac{\partial \rho_s}{\partial X_{cao}} \alpha_s Y_{s2} [\rho_g \alpha_g Y_{g3}]^{C_{eff}} \\
\frac{\partial s_{g4}}{\partial X_{cao}} &= \frac{\partial s_{g3}}{\partial X_{cao}} + \left(1 + \frac{M_{O_2}}{M_{SO_2}}\right) \frac{\partial s_{g2}}{\partial X_{cao}} \\
\frac{\partial s_{X_{cao}}}{\partial Y_{g2}} &= C_{s,1}\frac{\partial \rho_s}{\partial X_{cao}} \alpha_s Y_{s1} X_{CaO \rho_g \alpha_g Y_{g2}} + C_{s,1} \rho_s \alpha_s Y_{s1} \rho_g \alpha_g Y_{g2} \\
\frac{\partial s_{Y_{d1}}}{\partial X_{cao}} &= \left(1 - \frac{M_{CaSO_4}}{M_{CaO}}\right) \frac{\partial s_{X_{cao}}}{\partial Y_{d1}} \\
\frac{\partial s_{Y_{d2}}}{\partial Y_{d1}} &= \frac{\partial s_{Y_{d1}}}{\partial Y_{d1}} - \frac{\partial s_{Y_{d3}}}{\partial Y_{d1}} \\
\frac{\partial s_{Y_{d3}}}{\partial Y_{d1}} &= -\kappa_s \rho_g \alpha_g Y_{g1} + \kappa_s \alpha_s \rho_g Y_{g1} \\
\frac{\partial s_{g2}}{\partial \alpha_s} &= C_{s,g2} \frac{\partial \rho_s}{\partial \alpha_s} Y_{s1} X_{CaO \rho_g \alpha_g Y_{g2}} - C_{s,g2} \rho_s \alpha_s Y_{s1} X_{CaO \rho_g Y_{g2}} \\
\frac{\partial s_{g3}}{\partial \alpha_s} &= -C_{s,g3} \rho_s \alpha_s Y_{s2}^{C_{eff}} [\rho_g \alpha_g Y_{g3}]^{C_{eff}^{-1}} \rho_g Y_{g3} + C_{s,g3} \rho_s \alpha_s Y_{s2} [\rho_g \alpha_g Y_{g3}]^{C_{eff}^{-1}} \\
\frac{\partial s_{g4}}{\partial \alpha_s} &= \frac{\partial s_{g3}}{\partial \alpha_s} + \left(1 + \frac{M_{O_2}}{M_{SO_2}}\right) \frac{\partial s_{g2}}{\partial \alpha_s} \\
\frac{\partial s_{X_{cao}}}{\partial \alpha_s} &= C_{s,1} \rho_s Y_{s1} X_{CaO \rho_g \alpha_g Y_{g2}} - C_{s,1} \rho_s \alpha_s Y_{s1} X_{CaO \rho_g Y_{g2}} \\
\frac{\partial s_{Y_{d1}}}{\partial \alpha_s} &= \left(1 - \frac{M_{CaSO_4}}{M_{CaO}}\right) \frac{\partial s_{X_{cao}}}{\partial \alpha_s} \\
\frac{\partial s_{Y_{d2}}}{\partial \alpha_s} &= \frac{\partial s_{Y_{d1}}}{\partial \alpha_s} - \frac{\partial s_{Y_{d3}}}{\partial \alpha_s} \\
\end{align*}
\]
Eigenvalues of matrix \((P + M)^{-1} A\) for gas and mixture solids are as the following:

\[
\lambda_g = \frac{u_g (1 + M_{\text{ref},g}^2) + \sqrt{u_g^2 (1 - M_{\text{ref},g}^2)^2 + \frac{4}{\alpha_g} M_{\text{ref},g}^2 \alpha_g^2}}{2}
\]

\[
\lambda_s = \frac{u_s (1 + M_{\text{ref},s}^2) + \sqrt{u_s^2 (1 - M_{\text{ref},s}^2)^2 + 4M_{\text{ref},s}^2 \alpha_s^2}}{2}
\]

\[
\frac{1}{M_{\text{ref},g}^2} = 1 + \frac{1}{\alpha_g} \frac{1 - M_{\text{ref},g}^2}{\alpha_g^2}
\]

\[
\frac{1}{M_{\text{ref},s}^2} = 1 + \frac{\rho_s}{\rho_g} \frac{1 - M_{\text{ref},s}^2}{M_{\text{ref},g}^2}
\]

\[
M_{\text{g}}^2 = \frac{\beta_g^2}{\alpha_g^2}
\]

\[
M_{\text{s}}^2 = \frac{\beta_s^2}{\alpha_s^2}
\]

The algebra equations can be written as the following way.

\[
A_1(dw)_{i-1,j,k} + A_2(dw)_{i,j-1,k} + A_3(dw)_{i,j,k-1} + A_4(dw)_{i,j,k} + A_5(dw)_{i,j,k+1} + A_6(dw)_{i,j+1,k} + A_7(dw)_{i+1,j,k} = R_{i,j,k}
\]

where

\[
A_1 = -\frac{1}{2} \left[ A_{i-1,j,k} + |\Lambda| B_{i-1/2,j,k} \right]
\]

\[
A_2 = -\frac{1}{2} \left[ A_{i,j-1,k} + |\Lambda| B_{i,j-1/2,k} \right]
\]

\[
A_3 = -\frac{1}{2} \left[ A_{i,j,k-1} + |\Lambda| B_{i,j,k-1/2} \right]
\]

\[
A_4 = \frac{1}{2} \left[ C_{i,j,k} + |\Lambda| B_{i-1/2,j,k} + |\Lambda| B_{i,j-1/2,k} + |\Lambda| B_{i,j,k-1/2} + |\Lambda| B_{i,j,k+1/2} + |\Lambda| B_{i,j+1/2,k} + |\Lambda| B_{i+1/2,j,k} \right]
\]

\[
A_5 = -\frac{1}{2} \left[ A_{i,j,k+1} - |\Lambda| B_{i,j,k+1/2} \right]
\]

\[
A_6 = -\frac{1}{2} \left[ A_{i,j+1,k} - |\Lambda| B_{i,j+1/2,k} \right]
\]

\[
A_7 = -\frac{1}{2} \left[ A_{i+1,j,k} - |\Lambda| B_{i+1/2,j,k} \right]
\]
\[
A_{i,j,k} = \left[ \frac{\partial F}{\partial V} \frac{\partial V}{\partial W} \right]_{i,j,k}
\]
\[
B_{i,j,k} = \left[ (P + M) \frac{\partial V}{\partial W} \right]_{i,j,k}
\]
\[
C_{i,j,k} = \left[ \frac{P + M}{\Delta \tau} + \frac{M}{\Delta t} - \frac{\partial S}{\partial V} \frac{\partial V}{\partial W} \right]_{i,j,k}
\]
\[
\Lambda_k = \begin{bmatrix}
\lambda_{g,k} & 0 & 0 \\
0 & \lambda_{s1,k} & 0 \\
0 & 0 & \lambda_{s2,k}
\end{bmatrix}
\]  

(a-36)

Due to the source term on continuity equations is not zero, the species and momentum source terms modified as the following should be added to those equations.

\[
s_1 = Y_1 s_g
\]
\[
s_2 = Y_2 s_g
\]
\[
s_3 = Y_3 s_g
\]
\[
s_{g,2} = u_g s_{g,1}
\]
\[
s_{g,3} = v_g s_{g,1}
\]
\[
s_{g,4} = w_g s_{g,1}
\]

\[
s_{s,1} = Y_{s,1} X_{ca0} s_s
\]
\[
s_{s,1} = Y_{s,1} s_s
\]
\[
s_{s,2} = u_{s,1} s_s
\]
\[
s_{s,3} = v_{s,1} s_s
\]
\[
s_{s,4} = w_{s,1} s_s
\]

(a-37)
For gas species equations, the derivatives are as the following.

\[
\frac{\partial s_1}{\partial W_{1,1}} = \frac{s_2}{\rho g a_g}
\]

\[
\frac{\partial s_1}{\partial W_2} = Y_1 C_{s,g_2} W_{s,1}^1
\]

\[
\frac{\partial s_1}{\partial W_3} = Y_1 C_{s,g_3} \alpha_{s_2} C_{eff} \left[ W_3 \right] C_{eff}^{-1}
\]

\[
\frac{\partial s_1}{\partial W_4} = -\frac{Y_1}{p_g} s_g
\]

\[
\frac{\partial s_1}{\partial W_{s,1,1}} = \frac{Y_1}{\rho g a_g} s_g
\]

\[
\frac{\partial s_1}{\partial W_{s,1,21}} = \frac{Y_1}{\rho g a_g} s_g + Y_1 C_{s,g_3} \left[ W_3 \right] C_{eff}
\]

\[
\frac{\partial s_2}{\partial W_2} = Y_2 C_{s,g_2} W_{s,1}^1 + \frac{s_2}{\rho g p h a_g}
\]

\[
\frac{\partial s_2}{\partial W_3} = Y_2 C_{s,g_3} W_{s,21} C_{eff} \left[ W_3 \right] C_{eff}^{-1}
\]

\[
\frac{\partial s_2}{\partial W_4} = -\frac{Y_2}{p_g} s_g
\]

\[
\frac{\partial s_3}{\partial W_{1,1}} = \frac{Y_2}{\rho g a_g} s_g + Y_2 C_{s,g_3} \left[ W_3 \right] C_{eff}
\]

\[
\frac{\partial s_3}{\partial W_2} = Y_3 C_{s,g_2} W_{s,1}^1
\]

\[
\frac{\partial s_3}{\partial W_3} = \frac{s_3}{\rho g a_g} + Y_3 C_{s,g_3} \left[ W_3 \right] C_{eff} W_{s,21}^{-1} C_{eff}^{-1}
\]

\[
\frac{\partial s_3}{\partial W_4} = -\frac{Y_3}{p_g} s_g
\]

\[
\frac{\partial s_3}{\partial W_{s,1,1}} = \frac{Y_3}{\rho g a_g} s_g
\]

\[
\frac{\partial s_3}{\partial W_{s,1,21}} = \frac{Y_3}{\rho g a_g} s_g
\]
For gas momentum equations, the derivatives are as the following.

\[
\begin{align*}
\frac{\partial s_{g,2}}{\partial W_2} &= u_g C_{s,g2} W_{s,1}^1 \\
\frac{\partial s_{g,2}}{\partial W_3} &= u_g \frac{C_{s,g2}}{\rho_{s,2}} W_{s,21} C_{eff}^1 W_3^1 C_{eff}^{-1} \\
\frac{\partial s_{g,2}}{\partial W_{g,1}} &= -\frac{u_g}{\rho_g} s_g \\
\frac{\partial s_{g,2}}{\partial W_{g,2}} &= \frac{1}{\rho_g \alpha_g} s_g \\
\frac{\partial s_{g,2}}{\partial W_{s,1}} &= \frac{u_g}{\rho_{CaO} \alpha_g} s_g \\
\frac{\partial s_{g,2}}{\partial W_{s,21}} &= \frac{u_g}{\alpha_g \rho_{s,2}} s_g + \frac{u_g C_{s,g2}}{\rho_{s,2}} W_3^1 C_{eff}^{-1} \\
\frac{\partial s_{g,3}}{\partial W_2} &= v_g C_{s,g2} W_{s,1}^1 \\
\frac{\partial s_{g,3}}{\partial W_3} &= v_g \frac{C_{s,g2}}{\rho_{s,2}} W_{s,21} C_{eff}^1 W_3^1 C_{eff}^{-1} \\
\frac{\partial s_{g,3}}{\partial W_{g,1}} &= -\frac{v_g}{\rho_g} s_g \\
\frac{\partial s_{g,3}}{\partial W_{g,2}} &= \frac{1}{\rho_g \alpha_g} s_g \\
\frac{\partial s_{g,3}}{\partial W_{s,1}} &= \frac{v_g}{\alpha_g \rho_{s,2}} s_g + \frac{v_g C_{s,g2}}{\rho_{s,2}} W_3^1 C_{eff}^{-1} \\
\frac{\partial s_{g,3}}{\partial W_{s,21}} &= \frac{v_g}{\alpha_g \rho_{s,2}} s_g + \frac{v_g C_{s,g2}}{\rho_{s,2}} W_3^1 C_{eff}^{-1}
\end{align*}
\]

(a-39)
\[
\frac{\partial s_{g,4}}{\partial W_2} = w_g C_{s,g2} W_{s,1}^1 \\
\frac{\partial s_{g,4}}{\partial W_3} = w_g \frac{C_{s,g2}}{\rho_{s,2}} W_{s,21} C_{eff}^1 [W_3]^{C_{eff}^1-1} \\
\frac{\partial s_{g,4}}{\partial W_{s,1}} = -\frac{w_g}{\rho_s} s_g \\
\frac{\partial s_{g,4}}{\partial W_{s,2}} = \frac{1}{\rho_g \alpha_g} s_g \\
\frac{\partial s_{g,4}}{\partial W_{s,21}} = \frac{w_g}{\alpha_g \rho_{s,2}} s_g + \frac{w_g C_{s,g3}}{\rho_{s,2}} [W_3]^{C_{eff}^1} \\
\]

(a-40)

For solids-1 species equation, the derivatives are as follows.

\[
\frac{\partial s_{s,1}}{\partial W_2} = Y_{s,1} W_{s,1}^1 \left( 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right) \\
\frac{\partial s_{s,1}}{\partial W_{s,1}} = 2 Y_{s,1} C_{s,1} \left( 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right) W_{s,1}^1 \\
\frac{\partial s_{s,1}}{\partial W_{s,11}} = - \left[ Y_{s,1} \right]^2 C_{s,1} \left( 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right) W_{s,1}^1 
\]

(a-41)
For solids-1 momentum equation, the derivatives are as follows.

\[
\begin{align*}
\frac{\partial s_{s,12}}{\partial W_2} &= u_{s,1} C_{s,1}^1 \left[ 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right] W_{s,1}^1 \\
\frac{\partial s_{s,12}}{\partial W_{s,11}} &= u_{s,1} C_{s,1}^1 \left( 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right) W_2 \\
\frac{\partial s_{s,12}}{\partial W_{s,12}} &= -u_{s,1} Y_{s,1} C_{s,1}^1 \left( 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right) W_2 \\
\frac{\partial s_{s,13}}{\partial W_2} &= v_{s,1} \left[ 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right] W_{s,1}^1 \\
\frac{\partial s_{s,13}}{\partial W_{s,11}} &= v_{s,1} C_{s,1}^1 \left( 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right) W_2 \\
\frac{\partial s_{s,13}}{\partial W_{s,13}} &= -v_{s,1} Y_{s,1} C_{s,1}^1 \left( 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right) W_2 \\
\frac{\partial s_{s,14}}{\partial W_2} &= w_{s,1} \left[ 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right] W_{s,1}^1 \\
\frac{\partial s_{s,14}}{\partial W_{s,11}} &= w_{s,1} C_{s,1}^1 \left( 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right) W_2 \\
\frac{\partial s_{s,14}}{\partial W_{s,12}} &= -w_{s,1} Y_{s,1} C_{s,1}^1 \left( 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right) W_2 \\
\frac{\partial s_{s,14}}{\partial W_{s,14}} &= Y_{s,1} C_{s,1}^1 \left( 1 - \frac{M_{CaSO_4}}{M_{CaO}} \right) W_2
\end{align*}
\]