CPFD MODELING OF INDUSTRIAL-SCALE DRY FLUE GAS DESULFURIZATION SYSTEMS

James Parker, Ken Williams, Paul Zhao, Scott Thibault

CPFD Software, LLC, Albuquerque, NM, USA

Abstract – A reaction model was developed for the simulation of industrial-scale dry flue gas desulfurization (DFGD) systems using the CPFD method. The reaction model was validated in lab-scale simulations against experimental data for multiple temperatures and stoichiometric ratios. The applicability of the CPFD reaction model to industrial-scale systems was then demonstrated by the simulation of a large DFGD unit.

INTRODUCTION

The atmospheric release of SO_2 gas, a major contributor to environmental and health problems, can be substantially reduced by the use of flue gas desulfurization (FGD) technology in coal-fired power plants. Legislation in the United States and worldwide requires increasingly high levels of SO_2 removal, driving the need for efficient applications of FGD technology. While many technologies exist, the application, design, and optimization of FGD systems is dependent on the plant size, fuel source, and operating conditions.

The majority of FGD technologies use either a lime or limestone-based sorbent to react with the SO_2; however, the implementations of this chemistry in FGD systems are diverse. FGD systems are commonly classified as wet or dry systems – depending on the physical state of the sorbent when it is removed from the flue gas. In dry flue gas desulfurization (DFGD) technologies, the sorbent can be injected in a variety of possible locations within the power plant as an atomized slurry (lime spray drying, duct spray drying) or dry powder (furnace sorbent injection, duct sorbent injection). After sufficient contacting time, the sulfur-containing sorbent is later removed from the flue gas as a dried solid powder. For retrofits of burner systems, DFGD can be added directly into existing ductwork or as additional equipment for processing flue gas – design decisions that are influenced by the burner capacity, sulfur content in coal, and technology cost (Srivastava and Jozewicz, 2000).

Common design and operational requirements exist for DFGD implementations:

- *Mixing*: the injected sorbent must be well-mixed within the flue gas stream to ensure maximum desulfurization.
- *Residence time*: the sorbent must have sufficient contact time with the flue gas for sulfur reduction reactions and moisture evaporation, if necessary, to occur.
- *Temperatures*: consistent and appropriate operating temperatures are required for the reaction chemistry to occur as designed. For spray drying applications, temperatures must be within a range that allows the desired SO_2 reduction and while also forming a dry powder. For dry sorbent injection systems, the temperature must be high enough for rapid desulfurization reactions to occur yet below the threshold for sorbent deactivation or sintering.

The range of applications and factors affecting system efficiency create a need to better understand the operation of desulfurization systems. Computational fluid dynamics (CFD) has a long history of being used for this purpose and can play an important role in the design and optimization of new and retrofit FGD systems. Although CFD has been increasingly used in recent years to study DFGD systems (Zhang et al., 2007; Chang et al., 2011; Shi et al., 2011; Chen, 2012; Marocca and Mora, 2013), the need remains for accurate and efficient CFD models.

The discrete nature of droplets and particles is a defining physical characteristic of DFGD systems. Computationally, the use of an Eulerian-Lagrangian approach – in which particles and droplets are modeled as discrete Lagrangian points and the gas phase is modeled as an Eulerian continuum – is a natural choice. In this work, a CFD model has been developed to study the design and operation of DFGD technology in Barracuda Virtual Reactor® (Barracuda VR®), a commercial CFD software based on the Computational Particle Fluid Dynamics (CPFD®) method. The CPFD method is a computationally efficient Eulerian-Lagrangian CFD approach that has previously been used to model industrial-scale particle-fluid systems such as circulating fluidized bed combustors for biomass and coal (Weng et al., 2010; Snider et al., 2011; Blaser and Corina, 2012), fluidized catalytic cracking regenerators (Cha et al., 2012, Clark et al., 2012), polysilicon deposition reactors (Parker, 2011), and fluidized bed dryers (Parker et al., 2013). Study of large-scale systems in three dimensions with the CPFD method is enabled by use of the *computational particle* in

which particles with the same properties such as chemical composition, particle size, material density, and particle temperature are grouped together. This allows large commercial systems containing many billions ($\sim 10^{15}$ - 10^{16}) of particles to be analyzed using millions of computational particles without losing the advantages of discretizing the solid phase in a Lagrangian frame of reference. Details and development of the method are given by Andrews and O'Rourke (1996), Snider et al. (1998), and Snider (2001).

In addition to the modeling of the complex particle-fluid dynamics occurring in a DFGD system, it is necessary to also have an accurate model of the reaction chemistry occurring at the droplet or particle level in the DFGD system. For spray drying systems, reaction models have been proposed by Hill and Zank (2000) and Scala et al. (2004) which fully describe the desulfurization as a series of steps including diffusion of SO_2 in the gas phase to the droplet, diffusion of $Ca(OH)_2$ ions within the liquid droplet, and ionic reactions. For an industrial scale modeling, a reaction model ideally represents the controlling reaction rates and mass transfer resistances while maintaining computational efficiency.

REACTION MODEL

The overall reaction for a limestone-based desulfurization process is shown in Eq. (1).

$$SO_2 + Ca(OH)_2(s) \rightarrow CaSO_3(s) + H_2O \tag{1}$$

The reaction proceeds as a series of diffusion and reaction steps which have varying contributions to the overall reaction rate. In this work, the following assumptions are made:

- the desulfurization reaction occurs in the aqueous phase and the ionic reactions are very fast relative to the mass transfer limitations;
- the water in a droplet exists as a liquid film that surrounds a solid center;
- SO_2 diffuses from the bulk gas to the droplet surface where an equilibrium between the gas phase and aqueous phase SO_2 concentrations is maintained according to the temperature-dependent Henry's law constant;
- $Ca(OH)_2$ dissolves in the liquid at the solubility limit and diffuses through the liquid film to react with aqueous SO_2; and
- the formation of solid $CaSO_3$ does not hinder the transport of reactants to or from the reaction zones.

These assumptions are illustrated in the Fig. 1. As a consequence of these assumptions, the reaction rate is limited by the diffusion of SO_2 from the gas to the droplet surface and the diffusion of $Ca(OH)_2$ through the liquid film resulting in a strong dependence on the thickness of the liquid film and the rate of evaporation. As the liquid layer shrinks, the distance for $Ca(OH)_2$ diffusion also becomes smaller and the mass transfer rate is increased. The shrinking liquid layer also affects the surface area for SO_2 diffusion and the resulting reaction rate – the combination of the two mass transfer resistances – is constantly changing for the droplets up until the point at which the liquid film disappears completely and the desulfurization reactions cease.
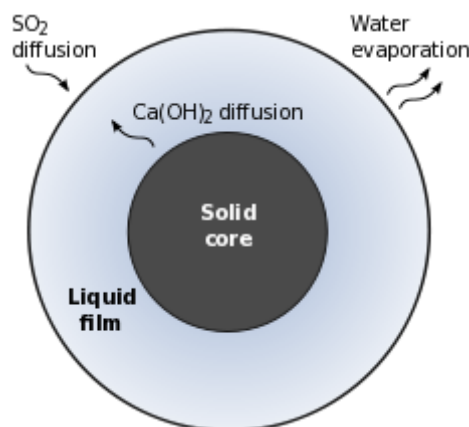

Fig. 1. Droplet level reaction model showing assumed locations of liquid film, solids, and diffusion.

An overall reaction rate combining the diffusional resistances for SO_2 and $Ca(OH)_2$ was derived starting from the general rate equation for mass transfer and reactions from Levenspiel (1999). This model is shown in Eq. (2),

$$r_{SO_2} = \frac{k_{g,SO_2} a_p [SO_2]_{gas} + \dfrac{k_{g,SO_2} a_p H \varphi}{RT} [Ca(OH)_2]_{aq}}{1 + \dfrac{H \varphi}{RT} \dfrac{[Ca(OH)_2]_{aq}}{[SO_2]_{gas}} + \dfrac{k_{g,SO_2}}{k_l} \dfrac{H}{RT}} \tag{2}$$

where $k_{g,SO_2} = Sh D_{SO_2,gas} d_p^{-1}$ and $k_l = D_{SO_2,liq} a_p \rho_{H_2O} m_{H_2O}^{-1}$. The Henry's law constant, H, is assumed to be equal to $1.213 \times 10^6 \exp(-2900K/T) \, [Pa \cdot m^3 \cdot mol^{-1}]$, based on data provided by NIST (2013). Furthermore, the maximum aqueous phase concentration of $Ca(OH)_2$ is assumed to be constant at 13.5 mol/m^3, which is the water solubility of $Ca(OH)_2$ at 75 °C.

A water evaporation model, previously used with the CPFD method by Parker (2013), is also included which assumes that evaporation is controlled by the mass transfer of water from the droplet surface to the bulk gas as shown in Eq. (3),

$$dm_{H_2O} / dt = k_{g,H_2O} a_p M_w \left([H_2O]_{gas} - \frac{p_{H_2O}(T)}{RT} \right) \tag{3}$$

where $k_{g,H_2O} = Sh D_{H_2O,gas} d_p^{-1}$. Although the evaporation rate is explicitly based upon mass transfer limitations, it should be noted that the temperature dependence of the particle pressure introduces strong thermal limitations to the evaporation model as well.

REACTION MODEL VALIDATION

The validity of the reaction model for desulfurization was confirmed by comparing simulation results using the reaction model with experimental data reported by Hill and Zank (2000) for the operation of a lab-scale spray dry absorber. The Hill and Zank data provides a thorough examination of critical factors affecting desulfurization: stoichiometric ratio between $Ca(OH)_2$ and SO_2, inlet gas temperature, and residence time. The lab-scale geometry consisted of a spray dryer (0.16 m inner diameter, 1.5 m height) at the top of which artificial flue gas containing 100 to 900 ppm SO_2 and 10 to 20 mol% water was introduced along with a liquid slurry containing 5 wt% lime that was sprayed through an atomizer. Flue gas and dried powder was collected at the bottom of the unit and analyzed.

The model of this experimental system was created in Barracuda VR version 16 to validate the derived reaction model. A diagram of the three-dimensional model along with selected views of the droplets, flue gas temperature, SO_2 levels, and flue gas water content is shown in Fig. 2. For all models, 5 wt% lime slurry was injected at a rate of 0.522 kg/hr with an initial droplet velocity of 50 m/s, diameter of 25 μm, and temperature of 25 °C. The flue gas contained between 200 and 900 ppm SO_2 and 15 vol% water entered at a rate of 17.9 kg/hr and a temperature of between 115 and 140 °C. All models were run until temperatures, gas compositions, and the inventory of injected droplets were stable after which the outlet gas composition data was time-averaged for comparison with experimental data.

A successful implementation of the reaction model with the CPFD method is demonstrated in Fig. 2. The data output, shown for a gas temperature of 140 °C and SO_2 concentration of 200 ppm (Ca/S = 2.7), illustrates the interactions between the water, flue gas, and temperatures in the system. As the droplets and flue gas are transported down the length of the absorber, with the predominant flow down the center of the absorber, the droplets rapidly lose moisture which shows up in the flue gas (far right image) and causes a decrease in flue gas temperature. Both the moisture level and temperature affect the desulfurization rate which in this case removed 66% of the incoming SO_2.

For comparison with the experimental data of Hill and Zank, the conversion efficiency, η, and stoichiometric ratio, λ, are defined as

$$\eta = \frac{N_{SO_2,in} - N_{SO_2,out}}{N_{SO_2,in}} \qquad \lambda = \frac{N_{Ca(OH)_2,in}}{N_{SO_2,in}} \tag{4}$$

where N_i is the molar rate of compound i. The efficiency at different stoichiometric ratios and temperatures is compared in Fig. 3 which shows that the reaction model applied to the CPFD method matches the experimental data extremely well. Most notably, the reaction model is capturing the decreasing efficiency at increased temperatures measured in the experimental results which is due to the faster evaporation of the liquid film on the droplet. Additionally, the model captures the transition from a low Ca/S operation

(Ca(OH)$_2$ limited) to a high Ca/S (SO$_2$ limited) indicating that the controlling resistances at the droplet level are represented reasonably well.
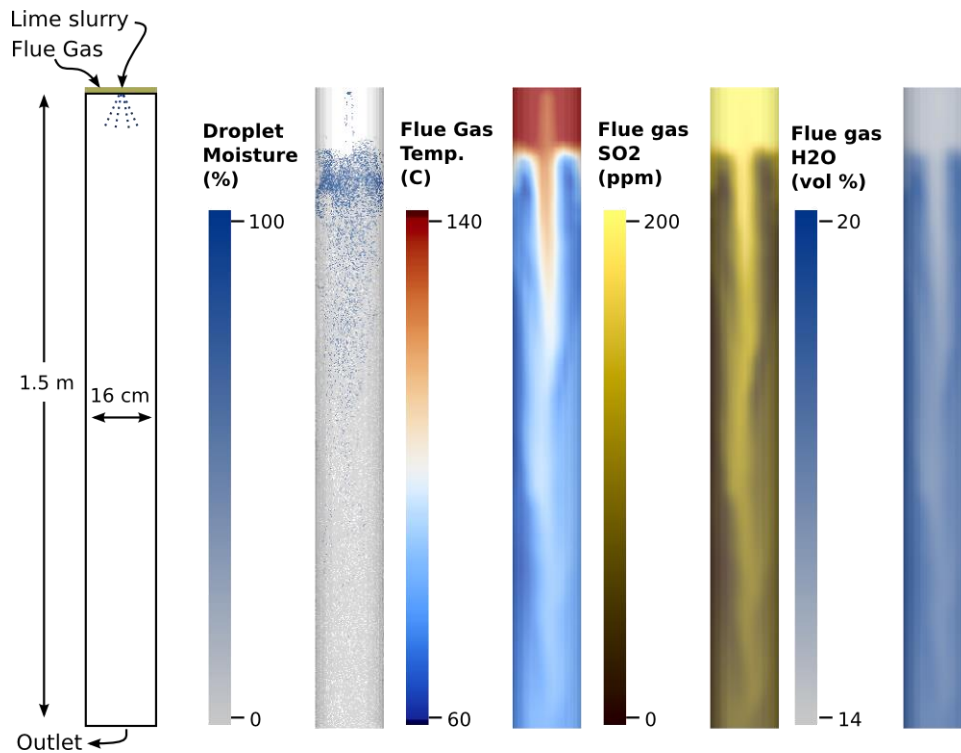

Fig. 2. Setup and selected results for inlet temperature of 140 C and Ca/S = 2.7
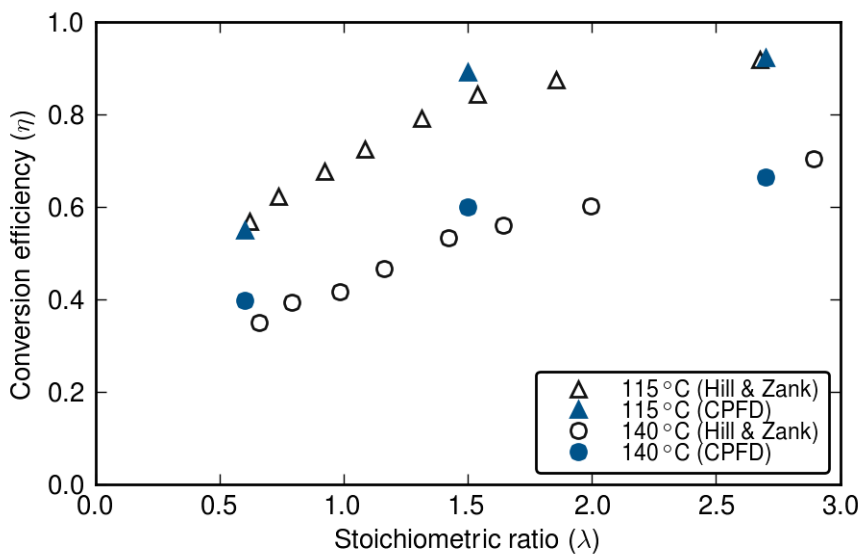

Fig. 3. Comparison of results using CPFD model and the experimental data of Hill and Zank (2000).

INDUSTRIAL-SCALE APPLICATION

The applicability of the reaction model to industrial-scale FGD systems was demonstrated by the incorporation of the reaction model in a large cyclonic flow spray drying absorber. As shown in Fig. 4, flue gas (20 kg/s, 15 vol% water, 200 ppm SO$_2$) at 115 °C is fed to the flue gas inlet and lime slurry (0.58 kg/s, 5 wt% Ca(OH)$_2$) is fed through an atomizer at the top center of the unit. The swirling flow created within the 11.6 m tall absorber is used to increase the residence time available for the desulfurization reactions to occur. The desulfurized flue gas and the dry sorbent powder leave the bottom of the unit. Analysis of time-average outlet gas of the simulation showed an 85% decrease in flue gas SO$_2$ and sorbent particles leaving the system on average with 10 wt% moisture. Examination of the simulation data in Fig. 4 shows a desirable performance of the unit. Particle moisture is maintained throughout the majority of the unit which allows the desulfurization reactions to occur to the fullest extent but prior to exiting the unit, particle moisture is

reduced to a level that is suitable to dry handling downstream. While further optimization is likely possible, these results clearly demonstrate the application of the CPFD model to an industrial-scale flue gas desulfurization system.
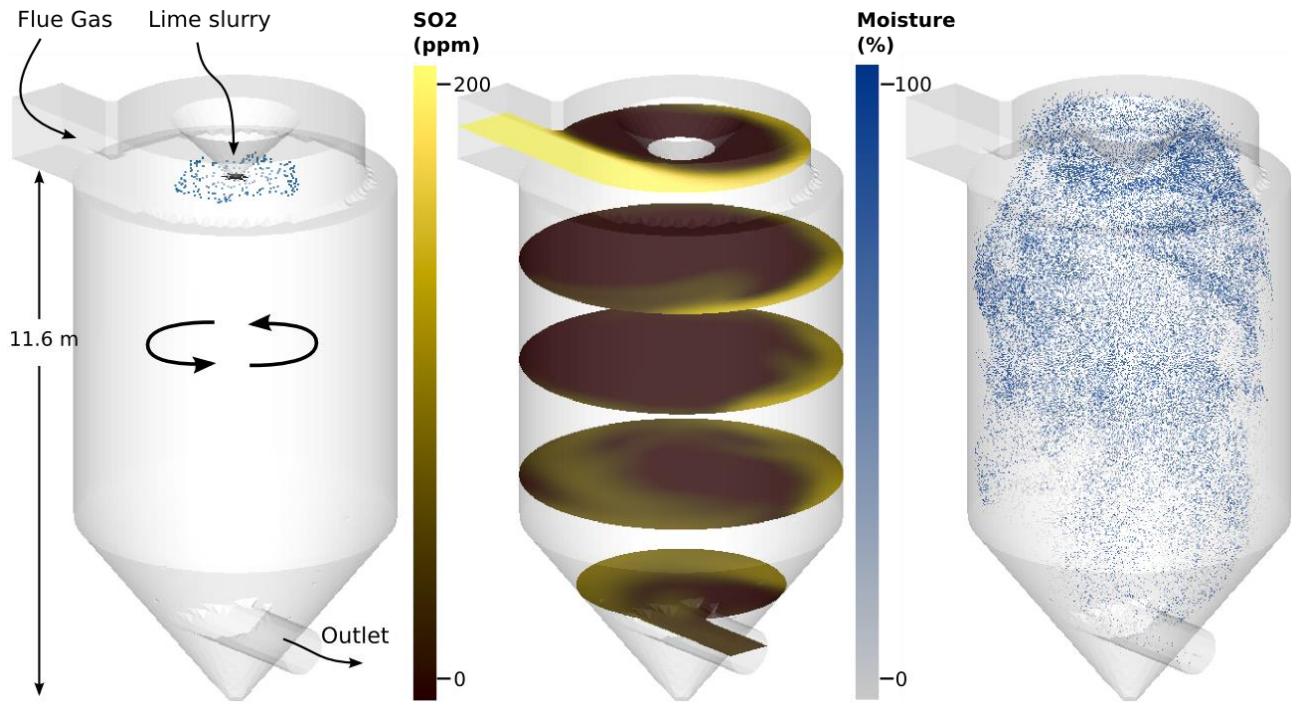

Fig. 4. Industrial-scale DFGD model: diagram of setup, SO_2 content, droplet moisture content

CONCLUSIONS

A reaction model was developed for modeling industrial-scale dry flue gas desulfurization systems using the CPFD method. A model of the experimental setup reported by Hill and Zank (2000) was created with the reaction model and the simulated results compared extremely well with the experimental data. The reaction model was subsequently incorporated into a CPFD model of large DFGD unit to demonstrate the use of the model for industrial-scale systems. Based on the success of this work, it is reasonable to believe that the use of the proposed reaction model and the CPFD method can be a valuable tool for the design and optimization of future DFGD systems.

NOTATION

a_p	Surface area of droplet	k_l	Liquid phase mass transfer coefficient
d_p	Diameter of droplet		
$D_{H_2O,gas}$	Gas phase H_2O diffusion coefficient, $\left(5.054 \times 10^{-9}\,\mathrm{m^2 s^{-1} K^{-1.5}}\right)T^{1.5}$	m_{H_2O}	Mass of water on droplet
		$p_{H_2O}(T)$	Partial pressure of water
$D_{SO_2,gas}$	Gas phase SO_2 diffusion coefficient, $\left(2.7402 \times 10^{-4}\,\mathrm{m^2 s^{-1} Pa K^{-1.5}}\right)T^{1.5}P^{-1}$	r_{SO_2}	Desulfurization reaction rate
		R	Ideal gas constant
		Sh	Sherwood number
$D_{SO_2,liq}$	Liquid phase SO_2 diffusion coefficient, $\approx 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$	T	Temperature of droplet
		φ	Ratio of diffusion coefficients in liquid phase, $D_{Ca(OH)_2,liq}/D_{SO_2,liq}$
$D_{Ca(OH)_2,liq}$	Liquid phase $Ca(OH)_2$ diffusion coefficient, $\approx 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$		
		ρ_{H_2O}	Density of water
H	Henry's law constant for SO_2		
k_g	Gas phase mass transfer coefficient		

REFERENCES

Andrews, M. and O'Rourke, P. 1996 The multiphase particle-in-cell (MP-PIC) method for dense phase particulate flows. *International Journal of Multiphase Flow*. 22, 379-402.

Blaser, P. and Corina, G. 2012. Validation and Application of Computational Modeling to Reduce Erosion in a Circulating Fluidized Bed Boiler. *International Journal of Chemical Reactor Engineering*, Vol. 10, A51

Cha, B., Kim, J., Son, S., Park, D., and Il, M. (2012). CPFD simulation of fluidized bed flow in FCC regenerator. *Proceedings of the 22nd European Symposium on Computer Aided Process Engineering*. 1154–1157.

Chen, C., Li, F., and Qi, H. 2012. Modeling of the flue gas desulfurization in a CFB riser using the Eulerian approach with heterogeneous drag coefficient. *Chemical Engineering Science* 69, 659-668.

Clark, S., Snider, D., and Fletcher, R. 2012. Multiphase Simulation of a Commercial Fluidized Catalytic Cracking Regenerator. Presented at *2012 AIChE Conference*, Pittsburgh, PA.

Hill, F.F., Zank, J. 2000. Flue gas desulfurization by spray dry absorption. *Chemical Engineering and Processing* 39, 45-52

Levenspiel, O. 1999. *Chemical Reaction Engineering, 3rd Ed.* John Wiley and Sons, New York.

Marocca, L. and Mora, A. 2013. CFD modeling of the Dry-Sorbent-Injection process for flue gas desulfurization using hydrated lime. *Separation and Purification Technology*. 108, 205-214.

NIST, 2013. Sulfur Dioxide. *Chemistry Webbook*. Retrieved October 15, 2013.

Parker, J. 2011. Validation of CFD Model for Polysilicon Deposition and Production of Silicon Fines in a Silane Deposition FBR, *International Journal of Chemical Reactor Engineering*, Vol. 9, A40.

Parker, J., LaMarche, K., Chen, W., Williams, K., Stamato, H., Thibault, S. 2013. CFD simulations for prediction of scaling effects in pharmaceutical fluidized bed processors at three scales, *Powder Technology*, 235, 115-120.

Parker J. 2013. CFD Model for the Simulation of Chemical Looping Combustion. Submitted for publication to Powder Technology.

Scala, F., D' Ascenzo, M., and Lancia, A. 2004. Modeling flue gas desulfurization by spray-dry absorption. *Separation and Purification Technology*. 34, 143-153.

Shi, L., Liu, G., Higgins, B., Benson, L. Computational modeling of furnace sorbent injection for SO_2 removal from coal-fired utility boilers. *Fuel Processing Technology*. 92, 372-378.

Snider, D., O'Rourke, P., and Andrews, J. 1998. Sediment flow in inclined vessels calculated using multiphase particle-in-cell model for dense particle flows. *International Journal of Multiphase Flow*. 24, 1359-1382.

Snider, D. 2001. An incompressible three-dimensional multiphase particle-in-cell model for dense particle flows. *Journal of Computational Physics*. 170, 523-549

Snider, D.M., Clark, S.M., O'Rourke, P.J. 2011. Eulerian–Lagrangian method for three-dimensional thermal reacting flow with application to coal gasifiers. *Chemical Engineering Science* 66, 1285–1295.

Srivastava, R., Jozewicz, W. 2001. Flue Gas Desulfurization: The State of the Art. *Journal of the Air and Waste Management Association* 51, 1676-1688.

Weng, M., Nies, M., and Plackmeyer, J. 2010. Comparison between Measurements and Numerical Simulation of Particle Flow and Combustion at the CFBC Plant Duisburg. *5. Internationaler VGB-Workshop "Betriebserfahrungen mit Wirbelschichtfeuerungen 2010"*

Zhang, J., You, C., Chen, C., Qi, H., and Xu, X. 2007. Effect of Near-Wall Air Curtain on the Wall Deposition of Droplets in a Semidry Flue Gas Desulfurization Reactor. *Environmental Science and Technology*. 41, 4415-4421.