MODEL OF HEAT TRANSFER IN CIRCULATING FLUIDIZED BEDS APPLIED FOR CO_2 CAPTURE BY CALCIUM-LOOPING PROCESS

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ABSTRACT

The heat transfer to wall panels in the circulating fluidized beds applied for calcium looping process is investigated by the a mathematical model. The heat transfer between the furnace wall and the bed includes contributions from radiation, particle and gas convection, and gas conduction; these processes are highly coupled and interrelated. The energy and mass balance equations together with the equations that describe the hydrodynamics and heat transfer processes were implemented in MATLAB/Simulink. The model gives satisfactory predictions of the gas/particles to wall heat transfer coefficient for several sets of operating parameters. The simulation's results show that more than 85% of the carbonation/calcination reaction has occurred in the dense region of the fluidized beds.

NOMENCLATURE

a	[-]	Decay constant
A_t	[m^2]	Cross-sectional area of the reactor
C_{CO2}	[mol/m^3]	Average CO_2 concentration
$C_{CO2,eq}$	[mol/m^3]	Equilibrium CO_2 concentration
$c_{p,j}$	[kJ/(kg·K)]	Specific heat of phase j
c_c	[kJ/(kg·K)]	Specific heat of particles clusters
d_p	[m]	Particle diameter
D	[m]	Column diameter
e	[-]	Emissivity of the phase (c – particles cluster, l - lean particle, b-bulk)
f_c	[-]	The fraction of wall surface covered by particles
g	[m/s^2]	Gravitational acceleration constant
G_S^*	[kg/(m^2·s)]	Saturated flux of solids out of reactor
h_c	[kW/m^2·K]	The clusters particles convection heat transfer coefficients
h_l	[kW/m^2·K]	The lean particles convection heat transfer coefficients
h_{pg}	[kW/m^2·K]	Particle-gas heat transfer coefficient
h_{pw}	[kW/m^2·K]	Particle-wall heat transfer coefficient
$h_{rc/rl}$	[kW/m^2·K]	Radiative heat transfer coefficient of the cluster or of the lean particles phase
h_w	[kW/m^2·K]	Conduction resistance to the heat transfer
H_{gap}	[kJ/(m·s)]	Heat flux transfer through the gas gap
$H_{Rcalc/carb}$	[kJ/(m·s)]	Reaction heat for calcination and carbonation
H_{pg}	[kJ/(m·s)]	Heat flux transferred from particle to gas
H_{pw}	[kJ/(m·s)]	Heat flux transferred from particle to wall
$k_{calc/carb}$	[s^{-1}]	Kinetic constant of the carbonation/calcination reaction
k_{gw}	[kW/m^2·K]	Heat transfer constant through the gas gap
$k_{c/g}$	[kW/m^2·K]	Thermal conductivity of the particles cluster or of the gas
L_{dense}	[m]	Dense zone height
L_{lean}	[m]	Lean zone height
L_{total}	[m]	Column height
M_i	[kg/kmol]	Molecular weight of specie *i*
Nu	[-]	Nusselt number
Pr	[-]	Prandtl number
Q_j	[kg/s]	Mass flow of phase j
S_{calc}	[kg/(s^2)]	Source term for calcination process
S_{carb}	[kg/(s^2)]	Source term for calcination process
t_c	[s]	The cluster residence time
T_j	[K]	Temperature of phase j
T_w	[K]	Temperature of wall
T_b	[K]	Temperature of bulk
U_0	[m/s]	Superficial gas velocity
U_j	[m/s]	Velocity of phase j
U_t	[m/s]	Terminal velocity
$V_{G/S}$	[m^3]	Volume of gas or solid phase
W_t	[kg]	Solid inventory
x_i	[-]	Mass fraction of specie *i*
$x_{i,eq}$	[-]	Equilibrium mass fraction of specie *i*
ε_{sd}	[-]	Dense zone voidage
ε_s	[-]	Solid fraction/concentration in the reactor
ε_s^*	[-]	Saturation carrying capacity of gas/solid density
$\varepsilon_{s,e}$	[-]	Solid fraction at exit of reactor
ξ	[-]	Process cycles coefficient
δ_g	[-]	Width of gas gap
σ	[W/m^2·K^4]	Stefan-Boltzmann constant
ρ_l	[kg/m^3]	Lean particle density
ρ_g	[kg/m^3]	Gas density
ρ_p	[kg/m^3]	Particle density
μ	[Pa·s]	Gas viscosity
j	index	Gas or solid (particles)
i	index	Component: CO_2, O_2, N_2 from gas phase, and $CaCO_3$ and CaO from solid phase

INTRODUCTION

The increasing of the greenhouse gases concentration in the atmosphere is directly linked to climate change. The Intergovernmental Panel on Climate Change (IPCC) has defined seven main sectors that contribute the most to global greenhouse gas emissions: energy supply, transport, building, industry, agriculture, forestry and waste management [1,2]. Globally, the energy sector causes the most carbon dioxide emissions. Several options are investigated for mitigating the carbon dioxide emission from energy sector: use of renewable energies, use of nuclear energy, use of low carbon content fuel, increase the efficiency of fuel conversion, carbon dioxide capture and storage. For the next decades, the most of the world electric energy will come from fossil fuel power plants, which produce a large amount of greenhouse gas (CO_2), carbon capture and storage technologies seem to be a viable solution, to reduce CO_2 emissions [1].

One promising method of CO_2 capture for power plants is to use a cyclic calcination-carbonation reaction (calcium looping process). This technique can capture CO_2 from the flue gas of coal-fired power plant by utilizing two fluidized bed reactors (carbonator and calciner) [2,3]. In the carbonator CO_2 is captured from the flue gas with solid calcium oxide at around 650ºC. This forms calcium carbonate $CaCO_3$, which is then transferred to a fluidized bed regenerator, known as the calciner, where the carbonate is regenerated back to calcium oxide at around 950ºC. The regenerated CaO is returned to the carbonator for a new sorption cycle (Figure 1).

MATHEMATICAL MODELING

The high flow rates of CO_2 produced by power plants require sufficient residence times and a good gas–solid contact to achieve reasonable reactor sizes and economic feasibility. The temperature distribution inside of fluidized columns is importance for the formation and reduction of harmful species within the furnace. The circulating fluidized bed is characterized by a relatively uniform temperature along the furnace height, which is due to the thermal inertia of solid particles.

The aim of the present work is to investigate (in time and space), by mathematical modeling, the components profiles, temperature profiles and hydrodynamics aspects inside the fluidized beds applied for CO_2 capture by calcium-looping process. The energy and mass balance equations together with the equations that describe the hydrodynamics and model of heat transfer were implemented in MATLAB/Simulink. The balance equations of the developed mathematical model for fluidized columns are presented in Table 1 [4-6].

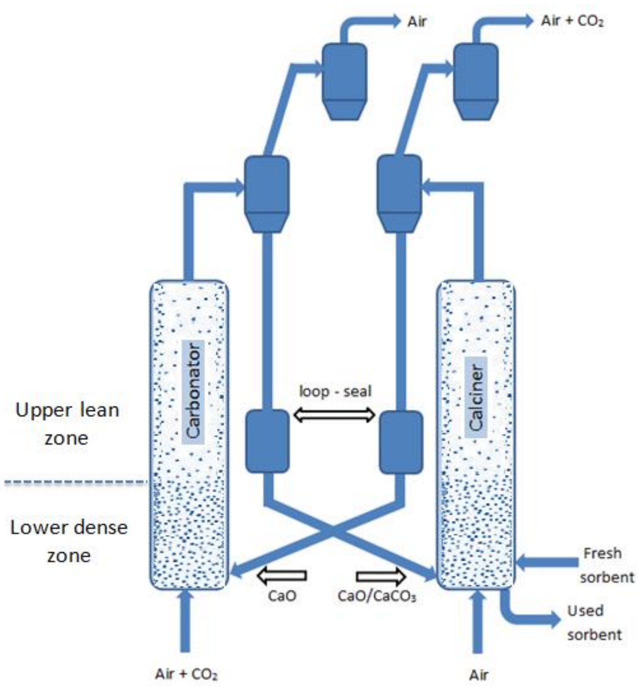


Figure 1 Calcium looping process [3]

Table 1 Reactors model equations

Continuity equations

$$\frac{dQ_j}{dt} = -U_j\frac{dQ_j}{dz} \pm S_{carb}/S_{calc} \quad (1)$$

Components mass balance

$$\frac{d[Q_j(x_i - x_{i,eq})]}{dt} = -U_j\frac{d[Q_j(x_i - x_{i,eq})]}{dz} \pm S_{carb}M_i \quad (2)$$

Energy balance

$$\frac{dT_j}{dt} = -U_j\frac{dT_j}{dz} + \frac{U_j(\pm H_{pg} - H_{pw} - H_{gap} - H_{R_{carb/calc}})}{Q_j c_{p_j}} \quad (3)$$

Reaction rate correlation for the carbonization (Grasa et al., 2008)

$$S_{carb} = \frac{\xi V_S k_{carb} Q_G (C_{CO_2} - C_{CO_2,eq}) M_i}{1000 V_G \rho_G} \quad (4)$$

Reaction rate correlation for the calcination (Garcia-Labiano et al.,2002)

$$S_{calc} = \frac{Q_S V_S}{U_S V_G} x_{CaCO_3} k_{calc} \frac{M_i U_j}{M_{CaCO_3}} \quad (5)$$

A reaction rate correlation for the calcinations reaction, S_{calc} (equation 4) presented by Garcia-Labiano et al. [7] and for the carbonization reaction, S_{carb} (equation 5) by Grasa et al. [3] was used in this work.

The energy balance equation of solid phase, is included: the convective flux in axial direction, the reaction term ($H_{Rcarb/calc}$), heat flux transferred from particles to gas (H_{pg}), heat flux transferred from particles to wall (H_{pw}), and heat flux transfer through the gas gap (H_{gap}). The equation of gas phase is included only the convective flux in axial direction and heat flux received from particles (H_{pg}).

Process hydrodynamics

The particle distribution within the circulating fluidized bed reactors, operating in turbulent transport regime is described according to the model proposed by Kunii and Levenspiel [8]. The fluidized reactors are divided into two regions: the dense region, in the lower part of the riser and the lean region where the volume fraction of solids decreases exponentially with height. In the bottom dense region the particles accumulate next to the wall limiting a core zone where the solid fraction of solids is low.

Knowing the dimensions of the reactor (L_{total}, D), solid inventory (W_t) and the volume fraction of solids at the reactor exit ε_{se} (equation 6), and in the reactor ε_{s*} (equation 7), it is possible to calculate the height of the lean zone L_{lean} (equation 8) and dense zone L_{dense} (equation 9).

The volume fraction of solids at the reactor exit ε_{se}, and in the reactor ε_{s*} was estimated according equation (6) and (7).

$$\varepsilon_{se} = \frac{G_s^*}{\rho_p \cdot (U_0 - U_t)} \quad (6)$$

$$\varepsilon_s^* = \frac{G_s^*}{\rho_p \cdot U_0} \quad (7)$$

The lean and dense zone heights are:

$$L_{lean} = \frac{1}{a} ln\left(\frac{\varepsilon_{sd}-\varepsilon_s^*}{\varepsilon_{se}-\varepsilon_s^*}\right) \quad (8)$$

$$L_{dense} = \frac{W_t}{A_t * \rho_s} - L_{lean}\left(\varepsilon_s^* + \frac{\varepsilon_{sd}-\varepsilon_{se}}{aL_{lean}}\right) \quad (9)$$

The following correlation was used to determine G_s^*:

$$G_s^* = 23{,}7 \cdot \rho_g \cdot U_0 \cdot exp\left(-5{,}4 \cdot \frac{U_t}{U_0}\right) \quad (10)$$

The terminal free-fall velocity U_T depends on the particle diameter d_p, solid and gas density ρ_s, ρ_g and the viscosity μ of the gas under the given conditions [8]. In the dense zone volume fraction of solids, ε_{sd} is constant and depends on the fluidization regime (U_0,) a value of 0.25 (and 0.16) was assumed.

Heat transfer

The cross-section of dense zone are commonly divided into two regions, with particles transported upwards in a dilute core, while a dense layer of solids in an outer annulus is assumed to descend along the wall [9]. Particles (clustered), after staying in the wall layer for an average residence length, are reentrained into the core and replaced by fresh particles that have the same temperature as the bulk. The heat transfer between the furnace wall and the bed includes contributions from radiation, particle and gas convection, and gas conduction. The heat transfer processes are illustrated schematically in Figure 2. As the wall layer descends, it loses heat to the gas by convection and gains heat from fresh particles due to core-wall layer particle exchange. Particles also participate in radiation from the core to the wall through the wall layer. The gas receives heat from the particles by convection and from the core by conduction. Heat is then conducted to the wall through the stagnant gas gap, and hence through the furnace wall [9, 10].

The heat fluxes transferred from particle to gas and wall (H_{pg} and H_{pw}) are described in equation (11) and (14).

- Particle-gas convective heat flux

$$H_{pg} = h_{pg} \cdot a \cdot (T_p - T_g) \quad (11)$$

The heat transfer coefficient for convective flow from particle to gas is:

$$Nu_{pg} = \frac{h_{pg} \cdot d_p}{k_g} = 2 + 1.8 \cdot \left(\frac{\rho_g \cdot (U_p - U_g) \cdot d_p}{\mu}\right)^{0.5} \cdot Pr_g^{1/3} \quad (12)$$

For spherical particles, the decay constant could be calculated by equation (13) [9]:

$$a = \frac{6 \cdot (1-\varepsilon)}{d_p} \quad (13)$$

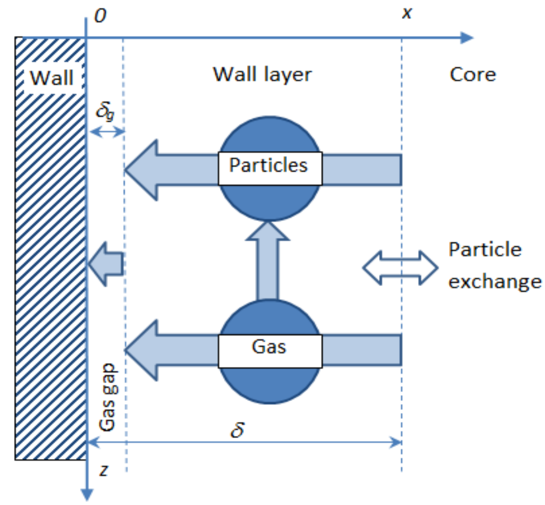


Figure 2 Schematic of heat transfer process [9]

- Particle-wall heat flux

$$H_{pw} = h_{pw} \cdot a_p \cdot (T_p - T_w) \quad (14)$$

where $a_p = \frac{4 \cdot (1-\varepsilon_c)}{D}$ (15)

The heat transfer coefficient for heat fluxes transferred from particle to wall is described according to the classical theory of Mickley and Fairbanks (1955) [11]:

$$h_{pw} = f_c \cdot (h_c + h_{rc}) + (1 - f_c) \cdot (h_l + h_{rl}) \quad (16)$$

The clusters particle convection heat transfer coefficients, h_c, The lean particles convection heat transfer coefficients h_l, can be expressed using equation (17) and (18).

$$h_c = \frac{1}{\left(\frac{k_c \cdot \rho_c \cdot c_c}{\pi \cdot t_c}\right)^{0.5} + h_w} \quad (17)$$

$$h_l = \frac{k_g \cdot Cp_p}{d_p \cdot Cp_g} \cdot \left(\frac{\rho_l}{\rho_p}\right)^{0.3} \cdot \left(\frac{Ut^2}{g \cdot d_p}\right)^{0.21} \cdot \mathrm{Pr} \quad (18)$$

The radiative heat transfer coefficients of the clusters h_{rc}, and of the lean phase, h_{rl} are depended by the specific emissivity of the phase: e_c and e_l and temperature of bulk and wall (Equation 19).

$$h_{rc/rl} = \frac{\sigma(T_w^4 - T_b^4)}{(T_w - T_b) \cdot \left[1 + \frac{1-e_{c/l}}{e_{c/l}} + \frac{1-e_b}{e_b}\right]} \quad (19)$$

- Heat flux transfer through the gas gap

$$H_{gap} = k_{gw} \cdot (T_g - T_w)/\delta_g \quad (20)$$

MODEL EVALUATIONS

The partial differential equations of the model were discretizated by spatial derivatives using first order approximations, and all mathematical equations have been implemented in MATLAB/Simulink.

The fluidization columns parameters [10] used in this work, (for 30 kW calcium looping test rig of INCAR-CSIC situated in Oviedo, Spain), are presented in Table 2.

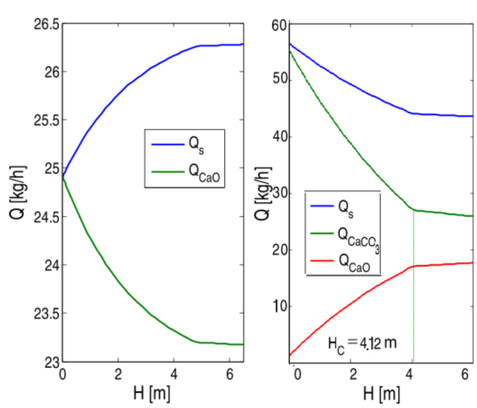
Table 2 The fluidization columns parameters

Parameter	Carbonator/Calciner
Mean particle size, dp [μm]	155
Height, L_{total} [m]	6.5/6
Diameter, D [m]	0.1
Gas velocity, U_0 [m/s]	1.1-3
Inlet CO_2 concentration, x_{in} [V/V%]	10
Temperature, T [K]	923/1023
Pressure, p [bar]	1
Solid fraction in dense region, ε_{sd} [-]	0.25

The mass balance of the developed model of CO_2 capture by calcium looping cycle has been validated with data collected from pilot plant published in literature, in a preview works [6]. A good correlation between carbon dioxide output concentration obtained by simulation and experimental had been observed, the R value is 0.98 [6].

Based on the total mass and component balance equations the steady-state profiles are given, in Figure 3, which represents the solid mass flow and CaO mass flow profiles in case of carbonator (Figure 3a) and calciner (Figure 3b). The discontinuity in the profile determines the end of the lower dense zone where the most part of carbonation/calcination process takes place. The simulation results show that more than 85 % of reactions have taken place in the dense region of the carbonator/calciner columns.

In terms of temperature inside the fluidized bed, this work simulation results show a uniform temperature along the fluidization column height, which is in line with the data published in the literature (Figure 4).



(a) (b)

Figure 3 Solid flows profiles
a) for carbonator and b) for calciner

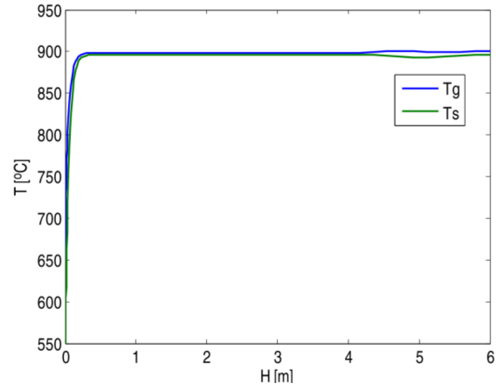


Figure 4 Solid temperature profile in calciner

The simulation results have showed that the height of the dense region decreases with increasing of the superficial velocity of the gas, from 4.72 m to 3.34 m for changing of gas velocity from 1 m/s to 2 m/s in carbonator case (Figure 5). Therefore at smaller superficial gas velocities much higher carbonation degree can be achieved.

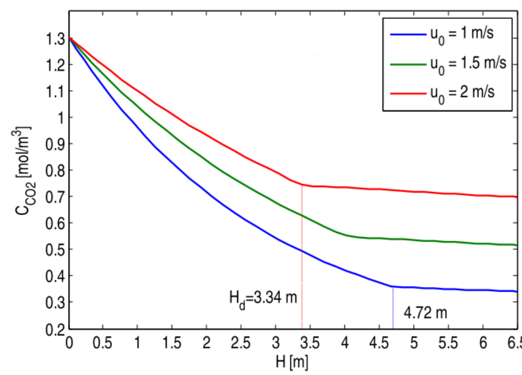


Figure 5 CO_2 concentration profile for carbonator for variable superficial gas velocity

CONCLUSIONS

The mass and energy balance equations together with the equations that describing the hydrodynamics of the process were implemented in MATLAB/Simulink. Temperature and composition profiles within the columns are predicted successfully by the model illustrating the predictive capabilities of the model. The simulation results suggest that the particles participate in a significant way in determining the radiation flux through the wall layer.

The most part of the chemical processes take place in the dense region; therefore the calcination/ carbonation rate is increasing with decreasing of superficial gas velocities.

The developed mathematical model can be used for analyzing CO_2 capture efficiency and understanding of micro level interaction of various processes taking place inside of circulating fluidized bed reactors.

ACKNOWLEDGMENTS

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