

## Dynamic Modelling of CO<sub>2</sub> Capture by Calcium-Looping Cycle

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Carbon capture and storage (CCS) technologies are mitigation measures aimed to reduce CO<sub>2</sub> emissions from energy and other energy-intensive sectors. Among various CCS technologies, chemical looping systems are considered as potential promising solutions to reduce CO<sub>2</sub> capture energy penalty. The paper presents a dynamic mathematical model of carbonation and calcination reactors of calcium-looping process to be used for carbon capture in fossil fuel-based power plants. The model described the particle distribution in carbonator / calciner according a 1D model for fast fluidization presented by Kunii and Levenspiel. The CO<sub>2</sub> adsorption efficiency in the carbonator is divided in two terms taking into account the dense and lean regions of the bed. The dynamic model evaluates the solid distribution gas velocity and particle diameter and predicts the overall CO<sub>2</sub> capture efficiency, taking into account that in every carbonation-calcination cycle the sorbent capacity decreases with the number of cycles.

### 1. Introduction

Climate change and global warming are caused by increased greenhouse gas emissions, mainly carbon dioxide resulted from human activity. Power generation sector which mostly uses fossil fuels (coal, lignite, natural gas etc.) is a major contributor to the increase of carbon dioxide concentration in the atmosphere and it consequently leads to global warming (IPCC, 2007). Carbon capture and storage (CCS) technologies are mitigation measures aimed to reduce CO<sub>2</sub> emissions from energy and other energy-intensive sectors (Vianello et al., 2012). However, the first generation of CCS technologies, i.e. scrubbing with amines, is energy intensive (Figueroa et al., 2008) and, thus, results in a substantial decrease in the overall plant efficiency (in the range of 10 net electrical percentage points – IPCC, 2007). To reduce the costs associated with the capture of CO<sub>2</sub>, 2nd and 3rd generation CCS technologies, such as carbonate looping or chemical looping combustion (CLC) have been proposed (IEA, 2012). For simplicity the carbonate looping and chemical looping combustion cycles are subsequently occasionally referred to as chemical looping cycles. The basic idea of the calcium looping process is to use calcium oxide as sorbent of CO<sub>2</sub>, through the theoretically reversible, reaction  $\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3$ .

The use of a Ca-based sorbent as a CO<sub>2</sub> acceptor was first patented in 1933 and assessed by other scientists for sorption-enhanced hydrogen production (Harrison, 2008), the application of a Ca-based sorbent in a post-combustion configuration was first proposed by Shimizu et al. (1999). In this configuration (Figure 1), carbon dioxide in the flue gas of a coal-fired power plant is captured by its reaction with calcium oxide in a fluidized bed reactor, carbonator and removed at high temperature from the gaseous phase by producing CaCO<sub>3</sub>. After heat recovery, decarbonized flue gas is vented to the atmosphere, while limestone converted back into CaO and gaseous CO<sub>2</sub> in other fluidized bed reactor, calciner (Charitos et al., 2011; Romano, 2012). The regenerated sorbent produced in the calciner is then returned to the carbonator for a new sorption cycle, while the CO<sub>2</sub>-rich gas is cooled and compressed for permanent storage after final purification. The high flow rates of CO<sub>2</sub> produced by power plants require sufficient residence times and a good gas–solid contact to achieve reasonable reactor sizes and economical feasibility (Alonso et al., 2009). However, the major challenge is the equipment design improvement and minimizing of the operating cost and investment.

Computational models can be valuable tools in the development of systems and processes. So, a detailed dynamic mathematical model, which describes each step of the process and takes into consideration the interaction between the carbonator and calcinator is necessary. The goal of this paper is to develop and validate against experimental data published in literature a dynamic model of the carbonator / calcinator of a Ca-looping process and to investigate the effects of different operating conditions on its performance.

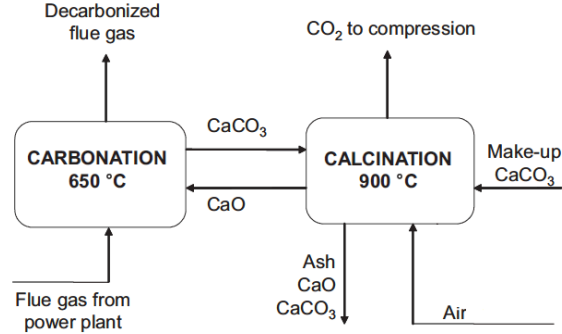


Figure 1: Scheme of the carbonate looping process

## 2. Mathematical modeling

### 2.1 The hydrodynamics of circulating fluidized beds

The particle distribution in the carbonator is determined by a 1D model for fast fluidization as presented by Kunii and Levenspiel (1990). In this model, the reactor is divided into two regions: the dense region, in the lower part of the riser, where the volume fraction of the solids,  $\epsilon_{sd}$  is constant, and the lean region where the volume fraction of solids decreases exponentially with height. In the dense zone,  $\epsilon_{sd}$  value depends on the superficial velocity  $u_0$  and the mean particle diameter  $d_p$ . Ranges of 0.2–0.4 (Kunii and Levenspiel, 1997) have been suggested and a value of 0.25 was assumed. Given the total reactor height  $H_t$  it is possible to calculate the height of the lean  $H_l$  and dense zone  $H_d$ , following the next four steps:

1. The mean particle size of the lime is known, therefore it can calculate the terminal free-fall velocity  $u_T$ , which depends on the particle diameter  $d_p$ , solid and gas density  $\rho_s$ ,  $\rho_g$  and the viscosity  $\mu$  of the gas under the given conditions (Kunii and Levenspiel, 1997).

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

$$u_T^* = \left[ \frac{18}{(d_p^*)^2} + \frac{0.591}{(d_p^*)^{1/2}} \right]^{-1} \quad (2)$$

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

2. The mass velocity of solids at the exit of the riser can be calculated from Eq(4) as a function of terminal velocity  $u_T$  and superficial gas velocity  $u_0$ , assuming spherical particles (Johansson et al., 2007).

$$G_s^* = 23.7\rho_g u_0 \exp(-5.5 \frac{u_T}{u_0}) \quad (4)$$

3. The volume fraction of solids at the reactor exit  $\epsilon_{se}^*$  could be determinate by following equation.

$$\epsilon_{se}^* = \frac{G_s^*}{(u_0 - u_T) * \rho_s} \quad (5)$$

$$\epsilon_s^* = \frac{G_s^*}{u_0 * \rho_s} \quad (6)$$

4. The height of the lean  $H_l$  and dense region  $H_d$  and mass of solids in each region  $W_l / W_d$  could be determinate using the following equations (Kunii and Levenspiel,1997), where  $A_t$  is cross-sectional area and  $au_0 = 4 \text{ s}^{-1}$ .

$$H_l = \frac{1}{a} \ln \left( \frac{\epsilon_{sd} - \epsilon_s^*}{\epsilon_{se} - \epsilon_s^*} \right) \quad (7)$$

$$W_l = A_t \rho_s H_l f_l, \quad W_d = A_t \rho_s H_d \varepsilon_{sd} \quad (8)$$

$$f_l = \varepsilon_s^* + \frac{\varepsilon_{sd} - \varepsilon_{se}}{H_l a} \quad (9)$$

## 2.2 Balance equations

The mathematical model of carbonator (Romano, 2012) and calciner (Cormos et al., 2005) is expressed by referring to an ideal plug-flow reactor and includes partial differential equations (PDE) to describe the time and space dependent parameters.

In case of carbonator, the total mass balance for the gas and solid phases are:

$$\frac{dQ_j}{dt} = -v_j \frac{dQ_j}{dz} \pm S_{carb} M_{CO_2} v_j \quad (10)$$

where:  $j$  represents solid or gas phase,  $v_j$  is the solid/gas velocity,  $Q_j$  is solid/gas flow,  $M_{CO_2}$  is the molecular mass of carbon dioxide,  $S_{carb}$  is the source term of  $CO_2$  from chemical reaction. The sign  $\pm$  shows the direction of  $CO_2$  mass transfer.

The component mass balance for the solid and gas phases are:

$$\frac{d[Q_j(x_i - x_{i,eq})]}{dt} = -v_j \frac{d[Q_j(x_i - x_{i,eq})]}{dz} \pm S_{carb} M_i \quad (11)$$

where:  $i$  is component:  $CO_2$ ,  $O_2$ ,  $N_2$  from gas phase, and  $CaCO_3$  and  $CaO$  from solid phase  $x_i$  – mass fraction of component  $i$ , in solid/gas phase,  $M_i$  is the molecular mass of component  $i$ ,  $S_{carb}$  is equal 0 for  $O_2$  and  $N_2$  component mass balance.

The model proposed by Grasa et al., (2008) which describes the reaction rate of cycled particles was used here. According to this model, the correlation which defines the carbonation degree  $X$  can be expressed according to a first order kinetic law where the kinetic constant  $k_r$  is a function of the carbonation degree it self. (Romano, 2012):

$$S_{carb} = \frac{\xi V_s k_{carb} Q_g (C_{CO_2} - C_{CO_2,eq})}{1000 V_g \rho_g v_g} \quad (12)$$

Where  $C_{CO_2}$  is  $CO_2$  concentration,  $C_{CO_2,eq}$  is equilibrium  $CO_2$  concentration. To express equilibrium pressure the equation proposed by Garcia-Labiano et al. (2002) is used (Eq13).  $\xi k_{carb}$  - is the kinetic and volume ratio between the potentially active solids ( $CaO$  and  $CaCO_3$ ) and the total solids (Romano, 2012).

$$p_{CO_2,eq} = 4.137 * 10^{12} \exp\left(-\frac{20474}{T}\right) \quad (13)$$

In case of calcinator, the total mass balance for the gas and solid phases are:

$$\frac{dQ_j}{dt} = -v_j \frac{dQ_j}{dz} \pm S_{calc} v_j \frac{M_{CO_2}}{M_{CaCO_3}} \quad (14)$$

And the component mass balance for the gas phase is:

$$\frac{d(Q_j x_i)}{dt} = -v_j \frac{d(Q_j x_i)}{dz} \pm S_{calc} v_j \frac{M_i}{M_{CaCO_3}} \quad (15)$$

where:  $S_{calc}$  is the source term from calcium carbonate decomposition reaction (is equal 0 for  $O_2$  and  $N_2$ ),  $M_i$  is the molecular mass of component  $i$ .

A reaction rate correlation for the calcinations reaction was presented by García-Labiano et al. (2002). Calcination reaction rate depends on the properties of the limestone and the relation of  $CO_2$  partial pressure  $p_{CO_2}$  to the equilibrium partial pressure

$$S_{calc} = \frac{Q_s V_s}{v_s V_g} x_{CaCO_3} k_{calc} \quad (16)$$

### 3. Results and discussions

All mathematical equations used in this model have been implemented in the equation oriented process simulator Matlab/Simulink 2008. The dynamic model of carbon dioxide capture by Ca-looping cycle has been validated with data collected from pilot plant, published by Charitos et al., (2011).

A summary of the fluidization columns characteristics and operating data, used in this work is presented in Table 1 (Charitos et al., 2011; Kunii and Levenspiel, 1997; Romano, 2012).

Table 1: Parameters of the model

Parameter	Carbonator	Calciner
Mean particle size, $d_p$ [ $\mu\text{m}$ ]	155	155
Height, $H_t$ [m]	6.5	6
Diameter, $D$ [m]	0.1	0.1
Gas velocity, $u_0$ [m/s]	1.1-2.5	1.1-2.5
Inlet $\text{CO}_2$ concentration, $x_{in}$ [V/V%]	10	0
Temperature, $T$ [K]	923	1173
Pressure, $p$ [bar]	1	1
Solid density, $\rho_s$ [ $\text{kg/m}^3$ ]	1660	1660
Inlet gas density, $\rho_g$ [ $\text{kg/m}^3$ ]	0.3956	0.2963
Solid fraction in dense region, $\varepsilon_{sd}$ [-]	0.25	0.25

Grasa and Abanades (2006) found a semi-empirical equation (Eq 17) to express the sorbent capacity after a large number of complete carbonation–calcinations cycles.

$$X_{max,N} = \frac{1}{1/(1 - X_r) + kN} + X_r \quad (17)$$

where  $k$  (0.52) and  $X_r$  (0.075) represent the deactivation constant and the residual conversion, respectively (Grasa and Abanades, 2006).

By combining the process model with an optimization algorithm using Grasa and Abanades semi-empirical equation and in accordance with experimental data published by Charitos et al., 2011, the  $\xi_{k_{carb}}$  values were estimated. In Figure 2, decay of the  $\text{CO}_2$  carrying capacity,  $X_N$ , vs. the carbonation/ calcination cycle number,  $N$ , for the Spanish limestone used by INCAR-CSIC and the German limestone used by IFK and value calculated by Grasa and Abanades correlation is presented.

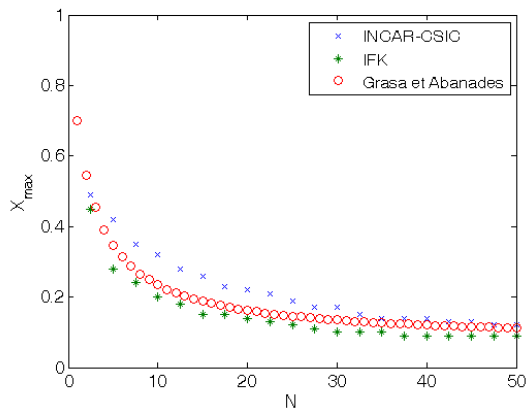


Figure 2: Sorbent conversion,  $X_N$ , vs. the carbonation/calcination cycle number,  $N$

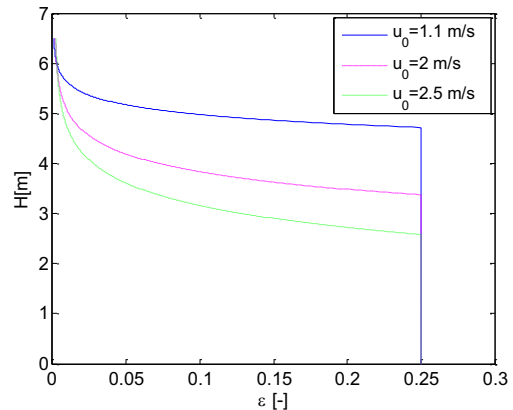


Figure 3: Vertical distribution of solid with variable superficial gas velocity

The superficial velocity of the gas has a major effect on the particle distribution in the turbulent fluidized bed (Kunii and Levenspiel, 1997). The height of the dense region decreases with the increasing of the superficial velocity of the gas (Figure 3). The most of the carbonation reaction takes place in the dense region, therefore at smaller superficial gas velocities much higher carbonation degree can be achieved.

The reliability of the carbon dioxide capture by Ca-looping process model was confirmed by comparing the data collected from model with experimental data published by Charitos et al. (2011). Some of the most representative data are presented in Table 2.

Table 2: Pilot plant data and simulated results

	N = 1		N = 5		N = 10		N = 20	
	exp	sim	exp	sim	exp	sim	exp	sim
$C_{CO_2,in}$ [mol/m <sup>3</sup> ]	1.3032	1.3032	1.3032	1.3032	1.3032	1.3032	1.3032	1.3032
$C_{CO_2,out}$ [mol/m <sup>3</sup> ]	0.3909	0.3552	0.7689	0.7496	0.8992	0.8955	1.0295	1.0148
X [-]	0.7	0.7274	0.41	0.4258	0.31	0.3128	0.22	0.2213

The most part of the carbonation reaction takes place in the dense region as can be seen from figure 4. In addition, more than 90 % of the total CO<sub>2</sub> capture is shown to occur the dense region of the carbonator, increasing the superficial velocity of the gas, the output concentration of the carbon dioxide decrease (Figure 4.a).

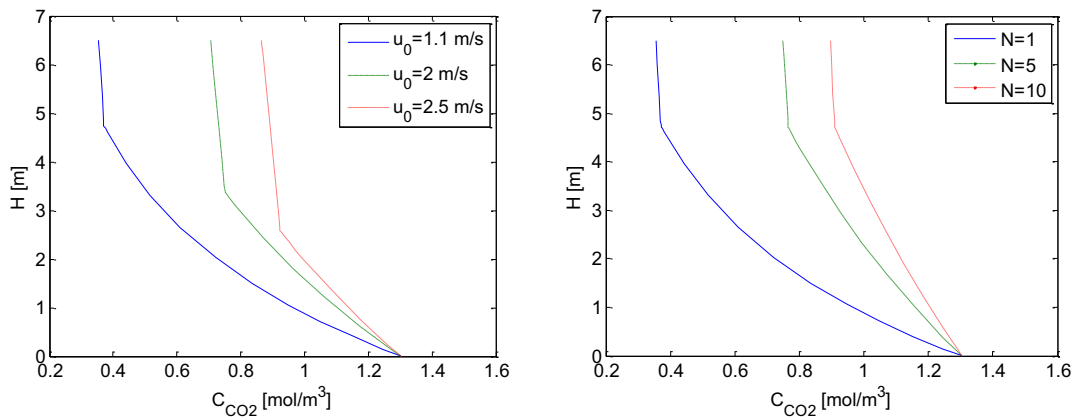


Figure 4: CO<sub>2</sub> concentration profile for carbonator: (a) for variable superficial gas velocity, (b) for variable carbonation/calcination cycle number

Figure 4.b presents the variation of carbon dioxide concentration with carbonation/ calcination number. In accord with experimental data, the model predicts that in every carbonation- calcination cycle the sorbent capacity decreases significant with the number of cycles.

The carbon dioxide mass fraction release from thermal decomposition of calcium carbonate and total gas flow (consisting to carbon dioxide flow from decarbonisation and carbon dioxide and air flow from fluidization gas) are presented in Figure 5.

As can be noticed from Figure 5, the carbon dioxide release in the calciner is taking place mainly in the dense region of the fluidised bed (as in the case of the carbonator reactor). Approximate 75 % of carbon dioxide is resulted in dense region of the fluidised bed.

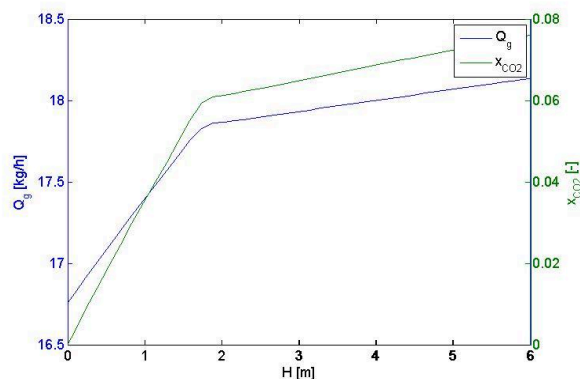


Figure 5: Gas flow profile and mass fraction of CO<sub>2</sub> release by decarbonisation process, for calciner

#### 4. Conclusions

The paper presents a dynamic mathematical model of carbonation and calcination reactors of calcium-looping process to be used for carbon capture in fossil fuel-based power plants. The developed model of CO<sub>2</sub> capture by Ca-looping cycle has been validated with data published in literature. The mathematical model described the particle distribution in carbonator / calciner according a 1D model for fast fluidization presented by Kunii and Levenspiel. The CO<sub>2</sub> adsorption efficiency in the carbonator is divided in two terms taking into account the dense and lean regions of the bed.

The developed model evaluates the solid distribution gas velocity and particle diameter and predicts the overall CO<sub>2</sub> capture efficiency, taking into account that in every carbonation-calcination cycle.

The simulation results was showed more than 90 % of the total CO<sub>2</sub> capture has occurred in the dense region of the carbonator. And 75 % of CO<sub>2</sub> is released into the dense region of the calciner. The height of the dense region decreases significantly from 4.2 m to 2.2 m with the increasing of the superficial gas velocity from 1.1 m/s to 2.5 m/s, for carbonator.

In terms of CO<sub>2</sub> capture efficiency, the model predicted that in every carbonation-calcination cycle the sorbent capacity decreases significant with the number of cycles, in accord with experimental data.

#### Acknowledgements

This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS - UEFISCDI, project ID PNII-CT-ERC-2012-1/2ERC: "Innovative systems for carbon dioxide capture applied to energy conversion processes".

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