

## 2<sup>nd</sup> Oxyfuel Combustion Conference

# Modelling and simulation of the carbonate looping process

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In this study carbonate looping process comprising of two interconnected fluidised beds is modelled. One-dimensional time dependent conservation equations for mass and energy are solved together with semi-empirical models for solid behaviour and heterogeneous reactions. Model gives information e.g. about the vertical profiles of gas components, solids materials and temperatures in the reactors. One dimensional dynamical models offer a powerful tool for evaluating the operation and performance of the carbonate looping process.

**Keywords:** carbonate looping process; 1D-dynamic modelling; CO<sub>2</sub> capture; chemical reactors

### 1. Introduction

With the growing demand of energy and abundance of some fossil fuels, interest has grown towards methods limiting stationary anthropogenic emissions from, for example, power plants burning coal. One promising method could be carbonate looping process. Carbonate looping process was first introduced by Shimizu [1]. The process utilizes the reversible reaction between calcium oxide and carbon dioxide,  $\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3$ .

Carbonate looping process comprises of two interconnected fluidized beds, carbonator and calciner, described at figure 1. Flue gases from the power plant flow to the carbonator where calcium oxide binds a large fraction of the CO<sub>2</sub> turning into calcium carbonate. The chemical reaction between calcium oxide and carbon dioxide is exothermic, excess heat from the carbonator can be used to benefit the steam cycle of the power plant. Solid material containing CaCO<sub>3</sub> and CaO is circulated to the calciner where CaCO<sub>3</sub> breaks into CO<sub>2</sub> and CaO generating a pure stream of CO<sub>2</sub>. Calcination reaction is endothermic and requires an external heat source. Studies have shown that oxycombustion of coal in the calciner would produce enough heat to sustain the reaction without large penalties for overall plant efficiency [2]. The air separation unit providing oxygen to the calciner would be much smaller than in a conventional oxy-fired boiler [3].

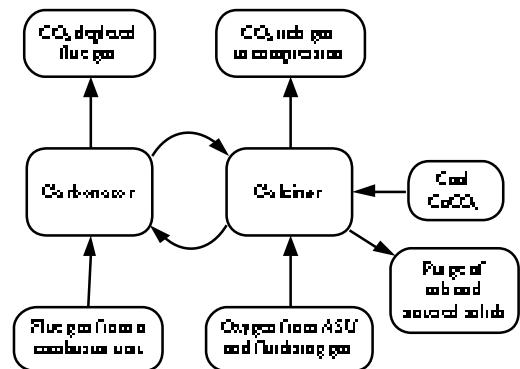


Figure 1. Description of the carbonate looping process

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Numerous studies have been done regarding the characteristics of this process, but no comprehensive one-dimensional models exist. Stationary 0-dimensional process models and reactor models have been created [4][5]. In this study, one-dimensional dynamic model frame has been developed allowing both steady state and dynamic analyses about the behaviour of carbonate looping units. The model will be applied to industrial scale analyses after the model has been validated with experimental results from smaller scale units. In this study, the model frame will be introduced and some results will be presented in order to describe the model capabilities.

## 2. Description of the modelling approach

Carbonate looping process relies on the fast reaction between calcium oxide and CO<sub>2</sub>. However, the fast reaction period is limited by the sintering of pores in the calcium oxide particle. After the pores are closed by calcium carbonate, reaction is controlled by slow diffusion through the product layer which is unsuitable for CO<sub>2</sub> capture purposes [6][7]. Describing this decay of carrying capacity is essential to the accuracy of the model. Natural limestone undergoing carbonation-calcination cycles quickly reaches an asymptotical conversion degree limit. In a mix of different aged limestone particles the conversion degree limit is defined as the averaged maximum conversion degree [8]. In the present work the carbonation reaction rate is modelled with a correlation presented by [4].

Another limiting factor of the carbonation reaction is the CO<sub>2</sub> partial pressure relation to equilibrium partial pressure. The optimal temperature of carbonation has been determined to be around 650 °C when treating flue gases of conventional coal fired power plants at atmospheric pressure in a fluidised bed environment [4]. When temperature rises, reaction kinetics improve, but equilibrium CO<sub>2</sub> partial pressure rises causing the reaction to slow down or change direction. When considering operation temperature, carbonator has a narrow operation window, which has to be taken account in the modelling and construction of large units.

Unlike the carbonation reaction, calcination reaction is not limited by the sintering of pores and is relatively faster than carbonation. Temperature of the calciner is limited to 900-950 °C because of the melting point of ash. A reaction rate correlation for the calcination reaction used in this study was presented by [9].

Studied carbonate looping process consists of two fast gas fluidized riser and solids return systems after the risers. In the model the risers are divided into necessary amount of 1-D elements in vertical direction. Time dependent balance equations for the mass and energy are written for each element. Elements are treated as ideally mixed control volumes. Solid and gas phases are calculated separately using the same average temperature for both phases. Reactors are considered as insulated systems with option for internal heat exchange surfaces. Set of time dependent equations are solved using ordinary differential equation solver at Simulink/Matlab® system. A steady state solution can be obtained by simulating in time to reach balance state. When only steady state analyses are needed the calculation can be speeded up by using equal artificial time constants in submodels of process phenomena.

The gas phase is modelled as an ideal gas mixture consisting of O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O. For each gas component at the element, the mass fraction is solved using the general time dependent mass balance. The source terms created by heterogeneous reactions between gas and solid phases are taken into account when calculating the gas mixture mass flow rates between the elements.

The solid phase consist two solid materials at both risers, namely CaO and CaCO<sub>3</sub>. Total solid volume fraction is modelled using empirical correlation to describe the hydrodynamics of the fast fluidized bed. The vertical density profile is modelled using correlation provided by Johnsson and Leckner [10]. At the current modelling approach the riser is divided into the core and wall layer regions. At the core region the solid material is moving upward and at the wall layer downward. Thickness and solid density of the wall layer are estimated based on the riser dimensions and fluidizing conditions.

In order to solve the time dependent temperatures of the elements, the energy equation of gas-solid suspension is formed with convective flows of solids and gas mixture, energy dispersion due to turbulent motion of solids, energy source from chemical reactions and heat transfer to internal heat exchangers, respectively. Convective flows are divided into gas and solid phases and treated separately. The following assumptions are made: phases have the same temperature, specific heat of solid is constant, and at the gas phase is incompressible.

### 3. Conclusions

Carbon capture efficiency of the carbonate looping process depends greatly on the operation conditions in the reactors. Temperature level and solid circulation rates are key parameters defining the reaction kinetics. Modelled profiles for gas volume fractions, temperature and solid volume fraction within the carbonator are presented in figure 2. When the other conditions are favourable for the process, the highest reaction rate will take place in the dense bottom region of the bed. Even temperature profile within the reactor is due to intense mixing of solids within the fluidised bed reactor.

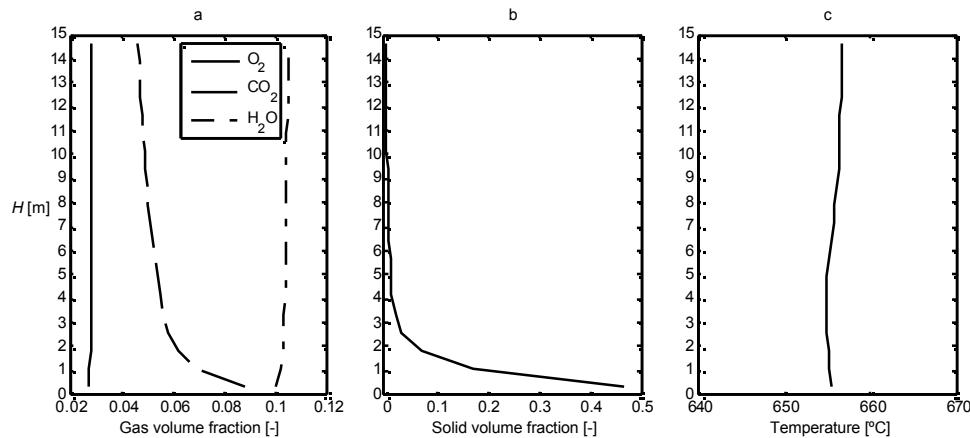


Figure 2. Simulations have been done with a fluidising gas mass flow of 0.4 kg/s,  $CO_2$  volume fraction 12 %, particle size 133  $\mu m$ , solid apparent density 1800  $kg/m^3$  and a solid inventory 1000  $kg/m^2$  in the carbonator. Carbonator has a diameter of 0.65 m and calciner 0.75 m and both reactors are 15 meters high. Temperature has been controlled in both reactors with a heat transfer surface. (a) Solid volume fraction (b) gas component volume fractions without nitrogen and (c) temperature within the carbonator as a function of height.

Behaviour of the process with two interconnected fluidised bed reactors is complicated and influenced by many control parameters, such as fluidising gas velocity, temperature and composition, as well as feed of fresh absorbent or solid fuel. Three-dimensional models can be used to analyze single reactors with radial effects but are computationally too heavy to analyze the overall process. One dimensional dynamical models offer a powerful tool for evaluating the operation and performance of the carbonate looping process.

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