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Energy Procedia 114 (2017) 242 – 249

Energy Procedia

13th International Conference on Greenhouse Gas Control Technologies, GHGT-13, 14-18 November 2016, Lausanne, Switzerland

Modelling a calciner with high inlet oxygen concentration for a calcium looping process

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Abstract

A calcium looping (CaL) process is a carbon capture technology which utilizes calcium oxide to remove carbon dioxide from the flue gas of a power plant. Like most capture technologies, CaL process has a high energy demand, which reduces power plant efficiency. The energy penalty and the operating and capital costs of the unit can be reduced by increasing the concentration of O_2 in the oxidant flow to calciner. In this study, a calciner has been studied with a three dimensional, steady-state, CFB process model. First, the model was validated by test data of the calciner in la Pereda CaL pilot. Next, a 3D model was created for a 200 MWth commercial scale calciner, in which the inlet oxygen concentration was increased up to 75% to map the potentials of improving the heat balance of the system and to investigate how the calciner operates in these conditions. Based on the simulations, the CaL process is feasible even at very high inlet oxygen concentration.

Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords: circulating fluidized bed; carbon capture; calcium looping; three-dimensional model

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Peer-review under responsibility of the organizing committee of GHGT-13.
doi:10.1016/j.egypro.2017.03.1166

1. Introduction

Greenhouse gas control and especially reducing of carbon dioxide emissions was one of the main topics in Paris Climate Change Conference in November 2015. In the agreement from this conference, the countries of United Nations agreed that the climate change is a threat to whole world and actions are needed to stop the global average temperature raise. Carbon capture and storage (CCS) is one option to reduce CO_2 emissions. The CO_2 can be captured before or after the combustion depending on technology. One promising post-combustion technology is the calcium looping (CaL) process where CO_2 is captured from the flue gas with irreversible carbonation-calcination reaction (1) which direction depends on temperature and partial pressure of CO_2 [1].

$$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} \qquad \Delta H_r^0 = -178\ \text{kJ/mol} \qquad (1)$$

CaL process utilizes natural limestone which is cheap and well known material as precursor of the CaO carrier material for CO_2 capture. The process system is usually comprised of two interconnected circulating fluidized bed (CFB) reactors: carbonator and calciner, Fig. 1. In the carbonator, the CO_2 from the flue gas is captured by calcium oxide (CaO) in the exothermic carbonation reaction. The reaction takes place at temperature below 700 °C in CO_2 partial pressure after typical air-fired combustion with coal. The formed calcium carbonate ($CaCO_3$) is then led to the calciner, where this solid material is regenerated back to CaO and CO_2 which is led out of the reactor to the purification and compression. The calciner needs an additional heat source to raise the temperature to around 900 °C, which is needed for the reaction and to cover endothermic calcination reaction heat requirement. Most obvious way to produce this heat is oxy-fuel combustion, which produces flue gas containing mostly CO_2.

The oxy-fuel combustion requires air separation unit (ASU), which causes significant energy penalty to power plant. One way to improve efficiency is to increase the oxygen concentration in combustion. The advantages from higher O_2 concentration comes from lower total gas flow to furnace which decreases the heat demand and cross-section area of the furnace. A smaller heat demand means smaller fuel input, which reduces the required oxygen flow. A smaller furnace decreases the investment cost of the plant and this is significant especially in CaL process, where the calciner is an insulated reactor.

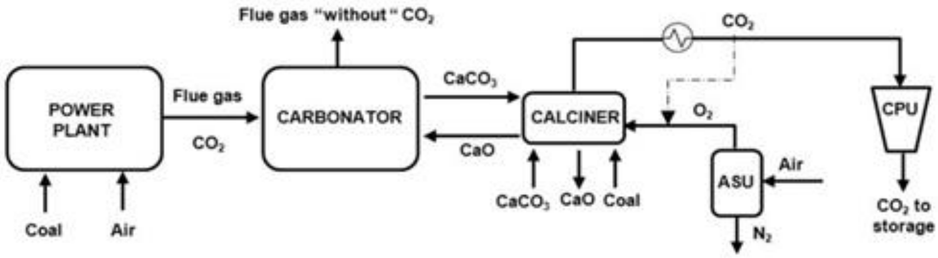

Fig. 1. Simplified process scheme of CaL process with high O_2 inlet to the calciner.

Oxy-fuel combustion is widely studied in PC and CFB boilers and higher O_2 concentration is a major development field [2]. In boilers, a high inlet O_2 concentration is challenging for heat recovery inside the furnace and the maximum level of O_2 is about 50 % [3]. In a calciner, the combustion heat is balanced by endothermic calcination reaction, which is occurring at same locations, where the combustion takes place. This provides a possibility to apply considerably higher O_2 concentrations.

The effect on plant efficiency with high oxy calciner concept has been presented in study by Romano [4] where the power plant steam cycle process is studied with the calcium looping process. In the study, oxygen concentration in oxidant was set to 50 %. In a small scale calcium looping testing, a 50 % oxygen concentration in oxidant flow to calciner has been reported at CANMET 75 kWth pilot-scale dual fluidized bed facility and IFK, University of Stuttgart, a 200 kWth dual fluidized bed facility for calcium looping tests [5,6].

In the present study, two different sized calciners were modeled in oxy-fuel combustion environment. First, a small scale calciner model was validated against results from la Pereda pilot facility calciner. A large scale calciner was then used to demonstrate calciner behavior with high oxygen concentration in oxidant gas.

2. La Pereda pilot plant

La Pereda calcium looping CO_2 capture pilot was commissioned in 2012. The pilot consists of two interconnected CFB reactors and the solid flow between reactors is controlled by double loop seals. The calciner can operate in air-fired mode by using a fan and in oxygen-fired mode by feeding a mixture of O_2 and CO_2 from tanks. The reactors are equipped with removable cooling bayonets for controlling the heat recovery. The test facility has been described in details by Sánchez-Biezma et al. [7] and CO_2 capture experimental results including oxy-combustion in calciner have been reported in [8-9] Since the commissioning, several test campaigns have been completed and the total operating time has reached more than 3100 hours. A comprehensive recent review of the experimental results is presented by Arias et al. in GHGT13-article titled “Operating experience in la Pereda 1.7 MWth Calcium Looping pilot”.

The pilot plant is integrated with la Pereda power plant, which is a 50 MWe CFB boiler firing bituminous coal. About 1/100 of the flue gas from the power plant is extracted after the electrostatic precipitator and fed to the carbonator for CO_2 removal. The carbonator can treat up to 2400 kg/h of flue gas, which is equivalent to about 1.7 MWth thermal input of the power plant. The firing capacity of the calciner varies between 1 – 3 MWth. The gases from the calciner and carbonator are returned back to the main flue gas path of the power plant after gas analyses.

3. Modelling

3.1. CFB3D model

The applied model has been originally created for simulating air-fired combustion in a circulating fluidized bed furnace. During recent decade, the model has been further developed to allow modelling of various CFB processes: air- and oxygen/steam-blown gasification, oxygen-fired combustion, bubbling fluidized bed combustion, and calcination/carbonation systems. In the model, the furnace or reactor is modeled three-dimensionally by control volume method to discretize and solve the various balance equations in a steady-state condition. The solved equations describe the different furnace phenomena: flow dynamics of gas and solids in Eulerian reference frame, reactions, comminution, and heat transfer. The particle size distribution and the comminution of solids is simulated by dividing all solid materials (e.g. ash, sorbents, char) to multiple particle size groups or fractions (usually six). The general concept of the model has been reported by Myöhänen and Hyppänen [10].

3.2. Cases

In the first case, a 3D model frame was built for La Pereda calciner. Results from pilot unit tests were used to validate 3D model parameters. The pilot unit calciner can operate both in air-fired and oxy-fired mode. This restricts the oxygen content in oxy-fired mode, which has to be close to oxygen content in air-fired mode to achieve proper gas velocity to reactor. The model frame of the pilot unit calciner has been presented in study by Ylätalo et al. [11]. The pilot unit calciner is cylindrical shape reactor which height is 15.2 meter and diameter is 0.75 meter.

The validation case is done in oxy-fired mode where oxidant oxygen concentration is 30.5 %. Air is used as secondary gas and for loop seal fluidization.

In the second case, a 3D model frame was built for a 200 MWth commercial size calciner. Calciner itself is considered to be a cylinder shape which diameter is 5.5 m and total height is 30 m. The cylinder shape has been chosen because the reactor has to be very well insulated to minimize the heat losses meaning that masonry reactor is the obvious choice. This shape is also providing better conditions for mixing between gas and solids compared to a rectangular shape boiler, which helps to avoid hot spots in the reactor. In the CFB3D model, the calculation mesh is structural with hexahedral calculation cells, thus, the reactor is not perfect circular form in model, Fig. 2. Total number of calculation cells is 42 008. The cyclone is modeled by setting separation efficiency to each solid and char fraction separately. The combustion reactions can take place also in the cyclone and the gas and solid temperatures can raise after reactor. The return leg distributes solid material back to calciner and to carbonator. The carbonator is modeled with 0D balance level to get proper input values for the calciner model.

The gas from ASU, which contain 95 % oxygen and 5 % nitrogen, is mixed with recycled flue gas and fed in the calciner as grid gas. Other gas inlets to reactor and return leg gas are set to feed recycled flue gas. The global oxygen concentration of input gas is 75 %. The main input values are presented in Table 1. The solid recirculation was set to 40 % to increase the solid material flow to calciner, which effectively level out the temperatures in CFB furnace. The solid material from carbonator is fed to one inlet which is located on opposite side of the cyclone. The fuel is mixed with calcium material and fed to same inlet to prevent hot spots appearing. The CaL process needs continuous fresh sorbent feed to system because natural limestone carrying capacity decreases in every cycle and sulfur from fuel reacts with calcium material reducing active CaO. The fresh sorbent is fed to the carbonator, which is simulated by a 0D-model.

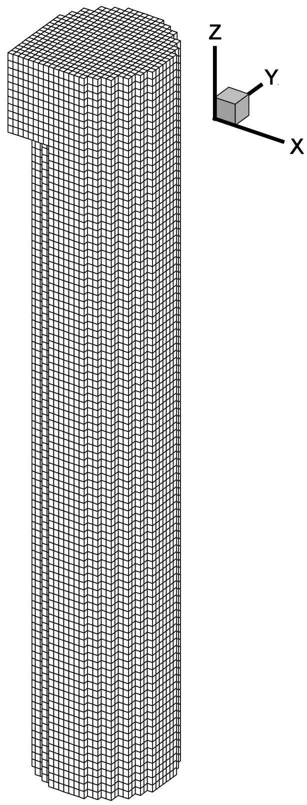

Fig. 2. Calculation mesh for 200 MWth calciner.

Table 1. Input values for 200 MWth large scale calciner.

Solid material flow from carbonator [kg/s]	275
Weight fraction of $CaCO_3$ [-]	0.193
Weight fraction of CaO [-]	0.630
Weight fraction of $CaSO_4$ [-]	0.046
Weight fraction of ash [-]	0.131
Fuel flow [kg/s]	8.34
Fuel HHV [MJ/kg]	25
Solid recirculation [-]	0.4
Gas flow to calciner [kg/s]	24.4
Input gas O_2 [vol-%]	74.9
Input gas CO_2 [vol-%]	16.9
Input gas H_2O [vol-%]	3.7
Input gas N_2 [vol-%]	4.5

4. Results

The calciner model for pilot scale La Pereda calciner was primarily used to validate key parameters related to chemical reactions and combustion. The validation case was calculated with 30.5 % oxygen concentration in the grid gas. The main interesting with 3D model focus on bottom region of the calciner, where the material is fed and the major proportion of the reactions takes place. As the figures illustrates, lateral gradients are very minor because of the narrow reactor. Some small local changes can be found near material feeding inlets: solid material from carbonator at the bottom and fuel feed at few meters high, Fig. 3. 3D result show that the pilot unit calciner could be assumed to be a 1D reactor where only vertical changes are important. The calcination reaction takes mostly place at the bottom of the reactor where the combustion is also highest. Thus, the heat source from the combustion reaction is balanced by the heat sink of the calcination reaction. This result motivated to test very high oxygen concentration in commercial scale calciner.

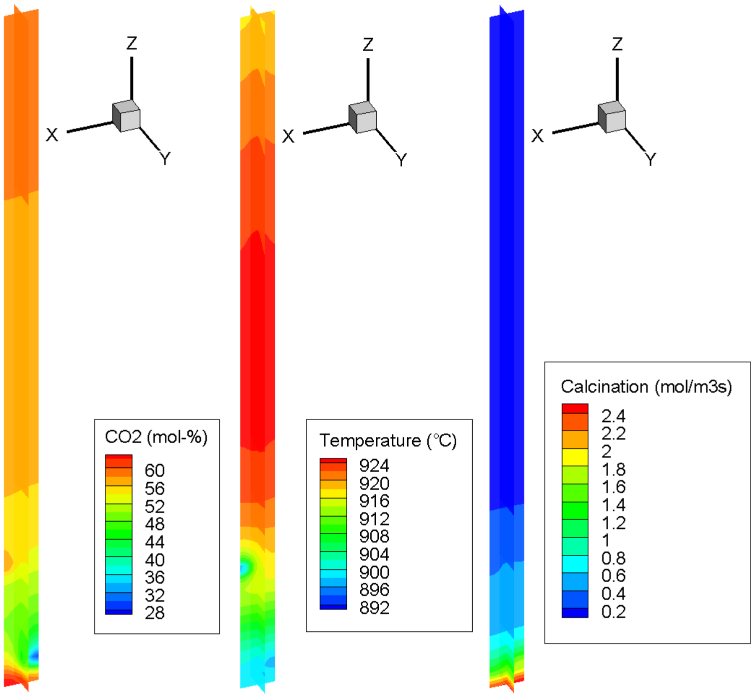

Fig. 3. Modelled CO_2, temperature and calcination contours of the pilot plant calciner.

As shown in Fig. 4, the 3D model agrees very well with the measured values. The measured temperatures inside the calciner are very close to modeled temperature profile which is averaged and plotted in 1D. This indicates that reaction rates are correct in the model. The modeled flue gas composition is also very close to measured composition (Fig. 4 (b)).

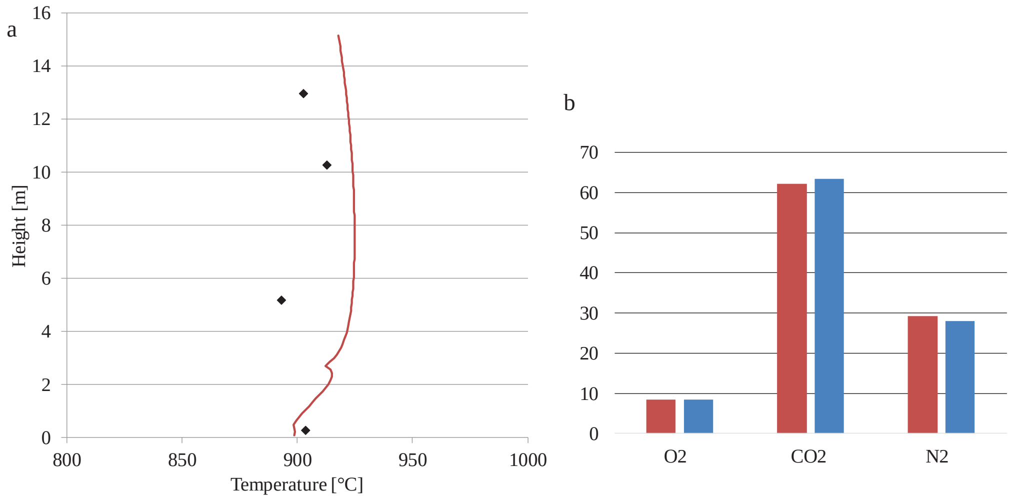

Fig. 4. (a) Modeled temperature profile and measured temperature points in pilot calciner. (b) Main components in dry flue gas are compared between CFB3D result (red) and measured data (blue).

In a large scale calciner, the 3D effects become more important. In Fig. 5, the inlet for solid material from carbonator is located at front, where the temperature is lowest and calcium carbonate share is highest. The temperature contour shows that temperature is around 900 °C in whole reactor area except near material feed inlet and no hot spots showed up. The CO_2 contour shows some lateral changes in all levels, which indicates the limited lateral mixing in large scale. This can be improved by modifying the design of the calciner. One improvement would be to share material more evenly in reactor area by adding material inlets. Sloped lower part could also provide better conditions for mixing.

The last contour plot, which illustrates the calcium carbonate share in sorbent, shows that the calcination is effective in the modeled calciner. In Fig. 6, all calculation cells temperature values are plotted as a function of local CO_2 partial pressure together with calcination curve. 78 % of all calculation cells are right side of the curve e.g. calcination side. The locations, which are on the carbonation side, are mainly found near the solid inlet, where the local temperature is lower. In the upper furnace, the temperature is above 880°C, thus, clearly on the calcination side, which leads to increasing CO_2 concentration towards the top of the reactor. The total calcination efficiency is about 85.7%, which can be further improved by enhancing the mixing of solids and gases in the reactor as previously described.

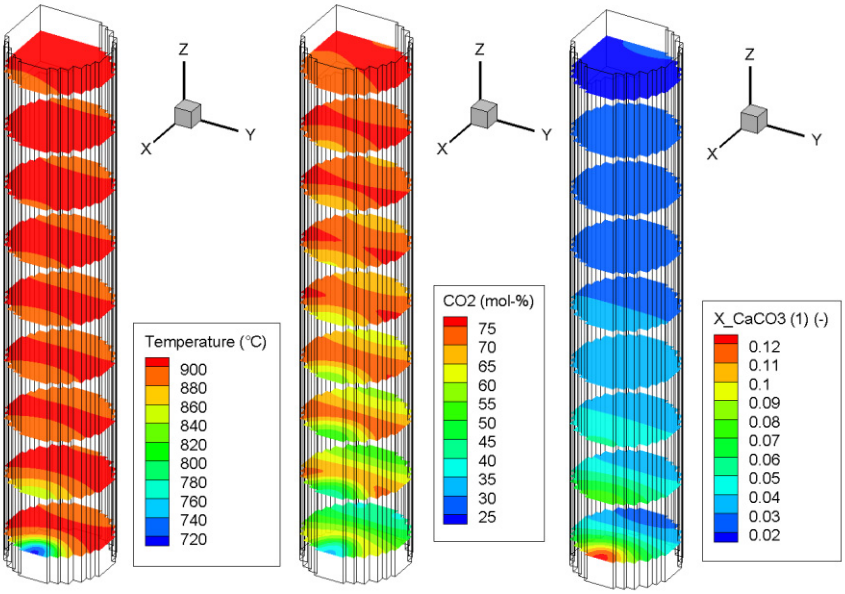

Fig. 5. Temperature, CO_2 molar fraction and calcium carbonate ($CaCO_3$) share in sorbent mass contours. Inlet for solid material from carbonator is located in front where temperature is lowest and $CaCO_3$ share is highest. Above material inlet the temperature and the $CaCO_3$ share are very uniform.

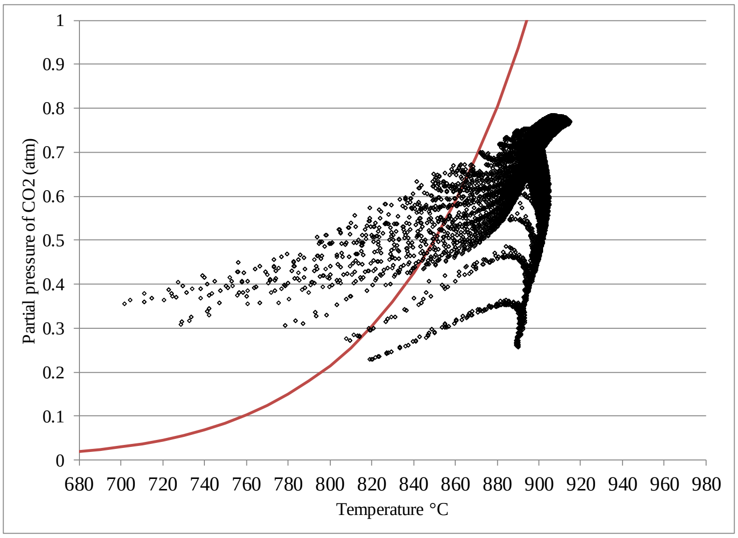

Fig. 6. Calculation cells temperature and local CO_2 partial pressure. Calcination curve show that values are mostly at calcination side.

5. Conclusions

CFB3D model was successfully used to model two different calciners. In the first case, the la Pereda 1.7 MWth pilot facility calciner unit was modeled and the results were compared with the measured values. The validation process was important to find proper parameters for model in this special CFB environment, where most of the solid material is reactive and the combustion heat is used to balance the endothermic reaction of calcination. The 3D results confirm that the calcination reaction is highest at the bottom of the reactor which should allow to increase the oxygen concentration in oxidant.

In the second case, the model frame was constructed for a large scale unit calciner. In that case, the oxygen concentration in oxidant was increased to 75% to study calcination and combustion in extreme conditions. Increasing the oxygen content is beneficial for the process by decreasing the heat need in the calciner and reducing the size of the calciner. The large scale calciner case results show that combustion stays in control and temperature is in proper level when using high oxygen concentration. The design of the calciner can be further improved to enhance mixing and to increase the calcination efficiency. Based on findings of the model studies, there are no technical limitations, which would prevent using even a higher inlet oxygen concentration for the calciner.

Acknowledgements

The work presented in this paper is being partially funded by the European Commission under the RFCS “CaO2” project.

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