CLEEN
Cluster for Energy and Environment

Research Report nr D338
Helsinki 2014

Jaakko Ylätalo, Tero Tynjälä

Calcium looping process design and retrofitting

ccsp
Carbon Capture and Storage Program

CLEEN LTD
ETELÄRANTA 10
P.O. BOX 10
FI-00130 HELSINKI
FINLAND
www.cleen.fi

ISBN XXX-XX-XXXX-X
ISSN XXXX-XXXX

Cleen Ltd.
Research Report nr XX

Jaakko Ylätalo, Tero Tynjälä

Calcium looping process design and retrofitting

ccsp
Carbon Capture and Storage Program

Cleen Ltd
Helsinki 2014

Report Title: Calcium looping process design and retrofitting

Key words: Calcium looping process, Concepts study, 250 MW retrofit case

Abstract

This report describes the calcium looping modelling work done as part of the CCSP-project by LUT Energia as subcontracting to Fortum Oy. The goal of this subcontracting package is to use the calcium looping models available at LUT to design and simulate a retrofitted calcium looping unit. An existing 1-D dynamic calcium looping model was applied to a large scale calcium looping concept capturing CO_2 from a 250 MWt power plant. The plant was dimensioned based on the experience from large CFB units and the heat transfer design was evaluated based on the initial simulations of the design case. The unit was then simulated in five load scenarios ranging from full load to no flue gas flow to the carbonator. The results from the simulations confirmed that the successful operation of a large scale calcium looping unit requires good heat transfer design including the cooling of the hot solids coming from the calciner. Also the recirculation of flue gas in both reactors is necessary to ensure sufficient fluidization for different particle sizes or flue gas flows from the source combustor. Solid circulation control is also critical because it affects heavily the thermal balance of the system as well as the capture efficiency and CO_2 balance. Utilizing the experience gained from large CFB-units coupled with new innovations, the scale-up of this process could be feasible in the near future. Further investigation of the solid mixing and temperature gradients in the carbonator and calciner bottom bed area with more detailed models like 3-D and CFD would confirm whether the capture efficiencies are as good as the 1-D model predicts.

Lappeenranta, March 2014

Table of contents

1 Introduction

This report describes the calcium looping modelling work done as part of the CCSP-project by LUT Energia as subcontracting to Fortum Oy. The goal of this subcontracting package is to use the calcium looping models available at LUT to design and simulate a retrofitted calcium looping unit. The reactors of the calcium looping system were dimensioned using initial calculations from a 0D-model and the dimensions and boundary conditions were implemented to the 1D calcium looping model framework. The 1D model framework was used to design heat transfer in the system, optimize solid mass flows between reactors, evaluate design point performance and produce 1D-profiles of process parameters from the reactors. The calcium looping system was also analyzed in partial flue gas loads where the flexibility of the system was studied. The main results of this subcontracting package have been published in Ylätalo et al. (2014).

2 Calcium looping process

Post-combustion calcium looping was first introduced by Shimizu et al. (1999). This technique can capture CO_2 and SO_2 from static sources by utilizing a twin fluidized bed system. Flue gas from a stationary source is processed in a fluidized bed reactor, known as the carbonator. The carbonator captures CO_2 and SO_2 from the flue gas to solid calcium oxide at around 650 ºC. This forms calcium carbonate and calcium sulphate, $CaCO_3$ and $CaSO_4$, which are then transferred to a fluidized bed regenerator, known as the calciner. The calciner regenerates the carbonate back to calcium oxide at around 920-950 ºC. The regenerated calcium oxide is returned to the carbonator where it resumes capturing CO_2 from the flue gases. The formed calcium sulphate is stable in the loop and will accumulate to the system unless fresh calcium carbonate is fed to the system and the used sorbent is removed at a steady rate. The temperature difference between the reactors can be achieved by many means, burning suitable fuels in the calciner in an atmosphere of oxygen and recirculation gas or from external heat sources. This forms a highly concentrated CO_2 gas flow which can be compressed and transported to a storage site after steam and oxygen removal. As a result of solid fuel combustion, ash accumulates in the system which increases the need of solid purging from the loop. The general layout of the calcium loop is presented in Figure 1.

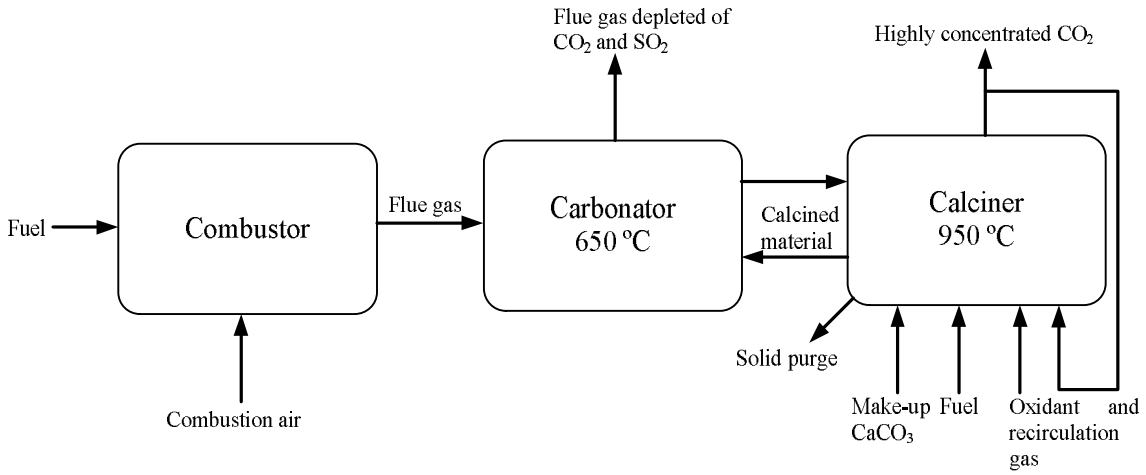

Figure 1. Concept of the calcium looping process.

3 The retrofit case

One of the biggest concerns of novel carbon capture units is their feasibility both technically and economically in large units. The feasibility of large units can be studied with modelling with low risk and effort. This study tries to map out the technical difficulties associated with large scale calcium looping units and provide practical solutions to the problems.

A conceptual power plant with a thermal power of 250MW was selected as the scale-up case. Several factors affected the size of the selected case. The pre-industrial size poses less financial risk but can be successfully extrapolated to a larger scale. Also the retrofitting with the calcium loop doubles the thermal output of the plant. General operation parameters of the power plant and the calcium loop are listed in Table 1 as well as the composition of the primary fuel and some essential simulation parameters. Currently the model can handle only one fuel so high quality coal is selected for the combustor and the calcium loop although power plants tend to use several fuels in combination. The calcium looping unit was modeled as a retrofit unit without steam cycle or thermal integration to the 250MW boiler.

Table 1. Retrofit case design point boundary conditions and parameters.

Parameter	Value
Combustor thermal power [MW]	250
Combustor fuel flow [kg/s]	8.333
Flue gas mass flow [kg/s]	115.92
Flue gas CO_2 [w-%]	21.16
Flue gas SO_2 [w-%]	0.17
Flue gas temperature [°C]	120
Designed capture efficiency [%]	80
Calciner fuel flow [kg/s]	9.229
Fuel LHV [MJ/kg]	30
Calciner thermal power [MW]	277
Carbonator cooling need [MW]	58
Oxidant flow [kg/s]	26
Make-up flow [kg/s]	11.15
Estimated maximum carrying capacity [w-%]	41
Fuel char [w-%]	67.6
Fuel volatiles [w-%]	22.5
Fuel moisture [w-%]	2.4
Fuel ash [w-%]	7.5
Average particle size [µm]	200
Average particle density [kg/m^3]	1800

3.1 Dimensioning of the reactors

The flue gas flow rate of the carbonator can be used to dimension the carbonator reactor once the average particle size is determined for the system. For the selected fuel and air-ratio of 1.2, the flue gas flow is 116 kg/s. Studies have shown that calcium looping systems tend to have a small particle size (<100 µm) due to fragmentation in the initial calcination and attrition in the looping (Gonzáles et al., 2010). With this particle size, it is quite difficult to operate in the conventional CFB-region. That is why it is more practical to use a higher average particle size commonly found in CFB-units. If the average particle size is fixed to 200 µm, the maximum superficial gas velocity can be set to 6 m/s. Both particle sizes are in the Geldart A class but the 100 µm particles approach the pneumatics transport region. A larger particle size could be achieved by using more durable limestone against fragmentation or increasing initial feed size. Calculating from the carbonator gas mass flow, approximate density and the maximum velocity, the cross section of the carbonator will be around 44 m^2. Because the gas velocity in the carbonator is decreasing due to the adsorption of CO_2 by the CaO, the use of sloped bottom section, commonly found in CFB boilers, is not appropriate. Also using secondary flue gas inputs is not necessary because that will only cause some of the flue gas CO_2 to bypass the dense, reactive part of the carbonator bed. The rectangle like cross section commonly used in CFB-boilers is not necessary but in order to keep structural integrity with the calciner, the carbonator width is determined to be the same as the calciner. The height of both reactors could be defined to maximize the residence time of gas and solids but in practice, the height the cyclone, standpipe and loop seal combination sets the maximum height of the system. In this case, a value of 35 m could be close to the reality when examining existing CFB boilers.

In the thermal design it was determined that an external heat exchanger would be the best solution to remove heat from the incoming solids from the calciner and carbonation reaction. An evaporator surface in the carbonator would be inflexible in terms of cooling in lower loads. Initial simulations also pointed out that, if the carbonator bed is refractory protected due to the very high erosion rate of the dense bed, the heat transfer rate in the bed is not enough to cool the solids to 650 °C. Using in-bed heat transfer tubes would quickly cool the solids but it would also lead to fast erosion of the tubes. Without pre-cooling of solids, the most reactive bed part would be outside of the equilibrium which would cause trouble in the capture. It was determined that the cooling the solids before feeding them into the carbonator would ease the heat transfer load in the carbonator bottom part. In addition, the equipment feeding the solids are also under great thermal stress and cooling of them is necessary. Location of external heat exchanger in the solid train feeding the carbonator is presented in Figure 2. In the model the external heat exchanger is executed by cooling the incoming solids to a low temperature (550–600 °C). In an actual unit, the external heat exchanger could receive solids from the carbonator to cool the reactor more efficiently due to the exothermic carbonation.

Calciner dimensions can be evaluated similarly keeping in mind that the calciner gas flow consists of the oxygen required for combustion, CO_2 from the recirculation gas and the CO_2 released from the calcination of $CaCO_3$ in the circulated material and make-up flow. A superficial velocity of 6 m/s in the freeboard was selected as a boundary condition and the fuel flow was defined from a simple 0D balance, with these assumptions the gas flow out of the calciner is around 108 kg/s. When the operation temperature is around 950 °C, the freeboard cross section is 60 m^2. The primary gas flow can be adjusted by reducing the amount of recirculation gas but it has to be kept in mind that the amount of oxygen in the gas should not be excessively high, because it could lead to too high combustion temperatures. In the calciner, a sloped section is necessary because the difference between the freeboard and grid gas mass flows is significant. By evaluating the grid gas mass flow and the exiting gas flow relation and the average time taken to reach the gas flow to fully develop, it was determined that the sloped section will be 5 m high and the grid cross section will be 43 m^2. With this dimensioning, the calciner velocity should remain constant along the reactor height. The width of the calciner was set to 3.8 m to keep the fuel, gas and solid penetration sufficient. Rectangular cross section commonly used in CFB-units was also selected for the calciner. This will set the length of the reactor to 15.8 m and the width of the grid section, 2.7 m, because the length is not changed in the grid. The carbonator width will be 3.8 m and depth 11.5 m and both reactors will be structurally connected at the ends Figure 2. This structural connection enables the construction of the solid return system alongside the reactor and the feeding of a portion of the solids back to the original reactor and transferring the remaining solids to the next reactor. The wall between the reactors is insulated to prevent heat transfer between reactors. Also this solid train type of solution enables the division of solid feeding along the reactor length to even out the active solid concentration in the reactor. This kind of solution can be modularized: larger units could be built by adding consecutive carbonator and calciner blocks, increasing the length. The main dimensions of the reactors and the thermal design solutions are listed in Table 2.

Table 2 Main dimensions of the reactors

Dimension (inner)	Carbonator	Calciner
Height of reactor [m]	35	35
Cross section of grid [m^2]	44	43
Cross section of freeboard [m^2]	44	60
Width of grid [m]	3.8	2.7
Width of freeboard [m]	3.8	3.8
Length [m]	11.5	15.8
End of sloped section height [m]	none	5
Elevation to exit channels [m]	33	33
Thermal design	External HE	Insulated

Both reactors are fitted with the ability to recirculate solids and gas. Solid and gas recirculation increases the flexibility of the unit as demonstrated in the results. The calciner is fluidized with the mixture of recirculation gas and oxygen. The carbonator can be fluidized solely with flue gas from the combustor or with a combination of recirculation gas from the carbonator or just with air.

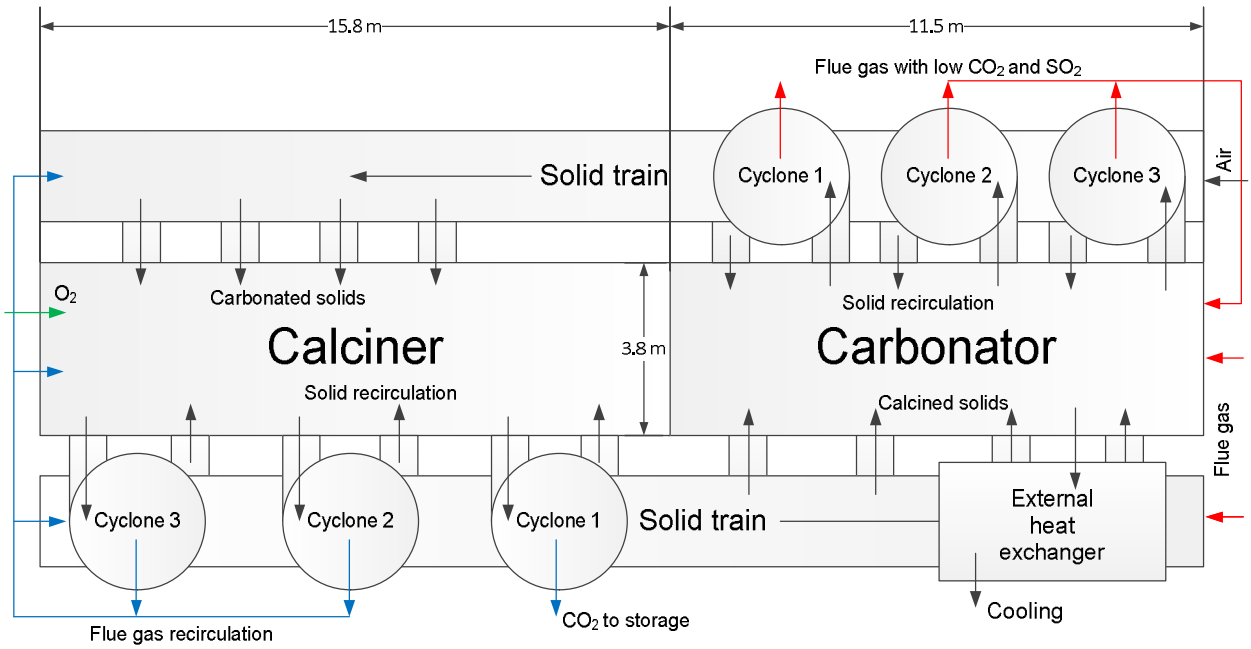

Figure 2. Simple dimensioning of the concept unit, with the external heat transfer block and solid/gas paths.

3.2 Main results of the simulations: design point-full load

The simulation results for the full load case and design point of the plant can be seen in Figure 3 to Figure 6. Figure 3 describes the overall balance of the system.

The performance of the system is higher than originally intended. The capture efficiency is 85 %, when the design value was 80 %. The sulphur capture is also almost 100% in both reactors. The fuel flow of the calciner has been evaluated to 9.23 kg/s which is equal to 277 MW thermal power. The ratio of the calciner thermal power of the total thermal power, $q_{calciner}/(q_{calciner}+q_{combustor})$, is around 53% in the full load.

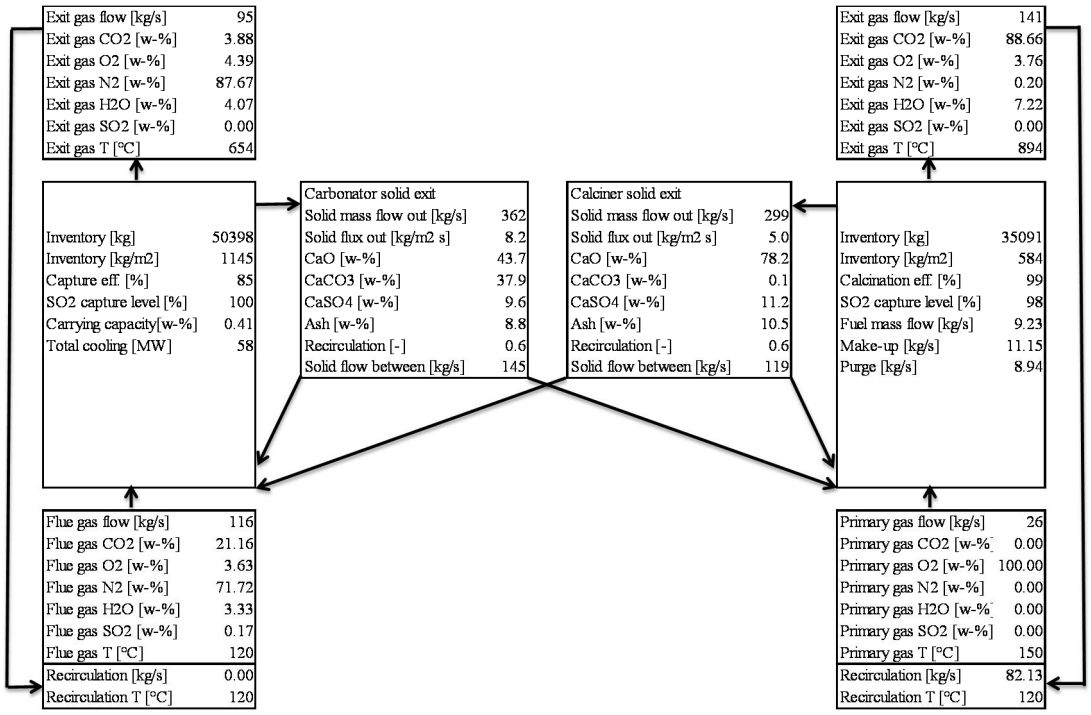

Figure 3. Overall balance of the full load calculation case.

The make-up flow for the case was determined based on the fuel ash and sulphur content, achieving an average carrying capacity of 41 w-% in the system. With the 6 m/s fluidization velocity, the solid mass flow out of the reactors is much larger than needed for moderate capture, and therefore 60 % of the solids is recirculated in both reactors. The fluidization velocity of the calciner is set to lower value than the carbonator velocity because it helps to control the overall solid inventory of the system. If the calciner velocity becomes higher and solids start to move to the carbonator, there is a danger that the whole reactor will be drained from solids. When the purge and solid control is on the calciner side, it is beneficial to keep the velocity difference favoring the calciner in other words higher velocity in the carbonator, Figure 4.

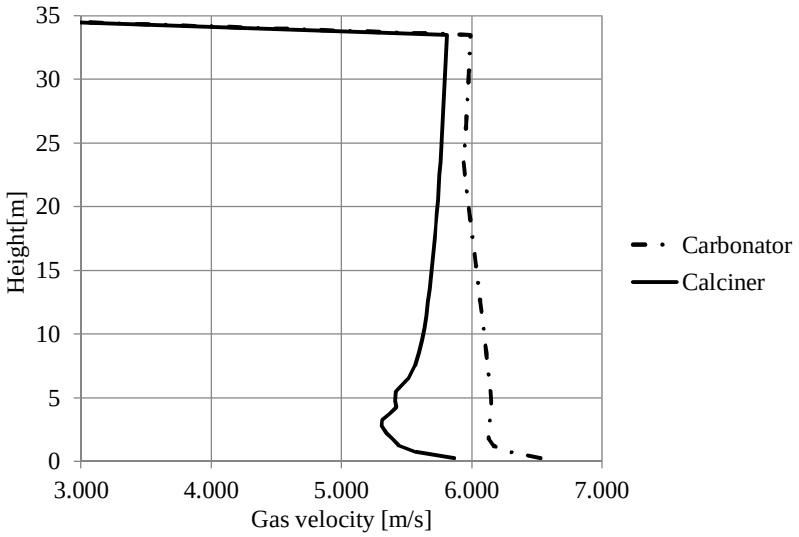

Figure 4. 1D velocity profiles of the reactors from full load calculation case.

Figure 5 displays the solid volume fraction profile and temperature profile of the carbonator. Especially from the temperature profile we can see that the temperature conditions are far from ideal even in the 1-D model. The entering solids are cooler than the objective temperature of the reactor. The total thermal power removed from the external heat exchanger and solid train is 58 MW.

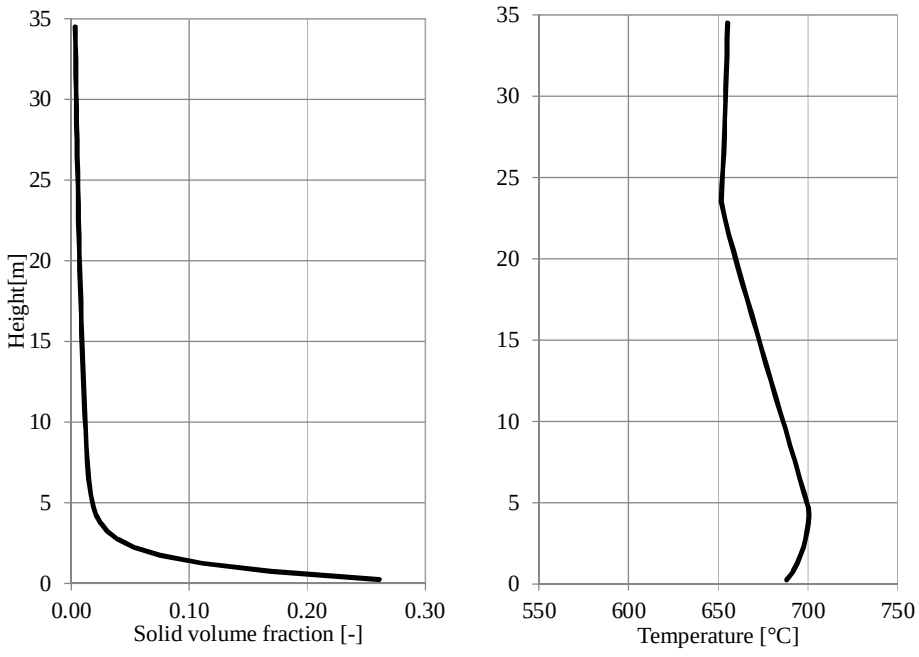

Figure 5. 1D solid volume fraction profile and temperature profile of the carbonator.

Figure 6 presents the corresponding solid volume fraction and temperature profiles for the calciner. Comparing the solid volume fraction profiles and calculated total masses of reactors, Figure 3, it can be seen that the carbonator has a higher inventory than the calciner which could be a result of the higher $CaCO_3$ content in the

carbonator. The average $CaCO_3$ concentration in the solids is quite close to the average activity achievable because recirculation increases the residence time of the solids in the reactor, displayed in Figure 3.

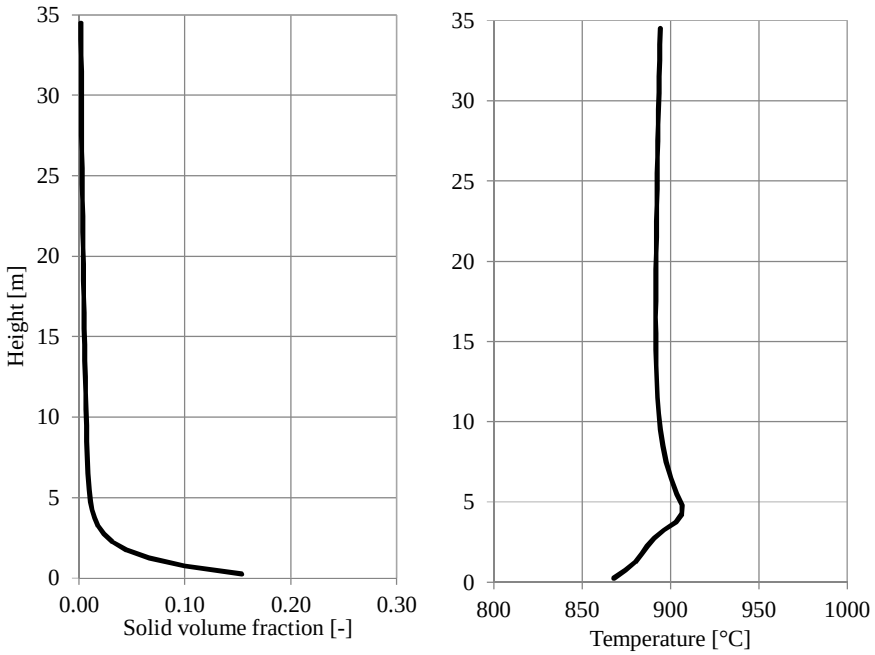

Figure 6. 1D solid volume fraction profile and temperature profile of the calciner.

Another interesting observation is that the calciner is running lower temperatures than the literature suggests. However, very good calcination efficiency is achieved. This could be a result of the lower CO_2 partial pressure in the calciner due to the flue gas recirculation, which increases the grid steam and oxygen partial pressures. The calcination model could overpredict the calcination reaction rate in the large-scale reactor. The average temperature in the 1D control volumes is quite close to the equilibrium temperature of the calcination reaction, which could cause some problems in a real unit because of the lateral temperature profiles present in a real large scale unit. In the temperature profile the insertion point of the cold solids can be seen as a drop of the temperature in the bottom region. Also the fuel insertion point close to the height of 5 m increases the local temperature by 50 °C. The calcination reaction is dominated by heat transfer because mass transfer effects are not significant with particles smaller than 300 µm (Martínez et al., 2013a), which means that in the calciner the solid material has a long time to react compared to the carbonator, in which it is critical to achieve good gas-solid contact in the dense bottom region of the reactor. In other words, the calciner operation is not so sensitive to local areas of temperatures below the calcination temperature in the lower part of the reactor.

3.3 Main results of the simulations: Partial load results

In the additional analysis of the system, the performance and behavior of the large scale calcium looping unit is analyzed in lower loads. In this context, the lower load means that the flue gas flow is lowered based on the power of the combustor where it is originating from. For example, the 75 % load means that the combustor is running at 75 % thermal power and the carbonator flue gas flow is updated based on that. The zero load scenario means that the power plant is shut down and no flue gas is available for the carbonator. The purpose of this zero load simulation is to demonstrate that the calcium looping unit can be run as an independent oxy-combustion power generation unit or a back-up power plant if the calcium looping unit is independent from the original combustor. Table 2 lists the input changes in different load scenarios.

All the other parameters were kept constant including the gas compositions and gas temperatures although they might change due to the changes in the combustor. The control scenarios have been devised based on the fluidizing conditions in the reactors. It was determined that achieving the CFB-mode becomes more difficult in the model when the fluidizing velocity drops below 4 m/s. From the 100 % to the 75 % load the adjustment can be done by means of lowering fluidizing velocities. Lower fluidizing velocity in the carbonator means a lower solid circulation rate and the calciner fuel and oxygen flow can be adjusted accordingly. When the CFB mode is not achievable anymore in the carbonator solely with the flue gas flow, the incorporation of the flue gas recirculation is necessary. In the calciner this is already present to dilute the oxygen flow. With both reactors equipped with the wet flue gas recirculation, a suitable fluidizing velocity can be achieved in different load scenarios. In the special case of the zero flue gas flow to the carbonator, the fluidization has to be handled with air. The flue gas recirculation has a positive side-effect, which is the increased CO_2 capture efficiency in the carbonator. However this comes with a price, because sustaining fluidization also requires maintaining some thermal power, which can be seen in Figure 7. This means that the relation of the calciner power to the combustor power increases in the lower loads, when in full power it is 53%, in the 30 % load it is 70%. The thermal efficiency of the loop increases a bit in the lower loads because less heat is needed for the make-up calcination or heating up the gas and solid flows. The thermal efficiency E_{thermal} of the system was approximated from equation

$$E_{\text{thermal}} = \frac{q_{\text{cooling}} + q_{\text{carb,gas}} + q_{\text{calc,gas}}}{q_{\text{fuel}}}$$

where q_{cooling} is the heat extracted from carbonator and solid train [W], $q_{\text{carb,gas}}$ is the heat captured from the gas stream leaving the carbonator and $q_{\text{calc,gas}}$ is the heat captured from gas stream leaving the calciner. The total thermal power of the calciner is q_{fuel}. The exit temperature of the carbonator and calciner gas flows was

selected to be 180 °C after the backpass heat exchangers to account for the dew point of sulphuric acid. This approach does not consider the performance of the backpass in lower gas flows. It very likely that the heat captured in the backpass is less in lower loads and the actual thermal efficiency is not higher in lower loads.

Table 2. Input changes for different load scenarios.

Parameter	Full load	75 % load	50 % load	30 % load	0 % load
Calciner inventory set [kg]	35091	35067	35050	35064	35042
Carbonator inventory (calculated) [kg]	50398	49548	47039	29220	19135
Flue gas flow [kg/s]	116	87	58	35	0
Oxidant flow [kg/s]	26	19	18	16	15
Fuel flow [kg/s]	9.23	6.92	6.20	5.90	5.50
Calciner flue gas recirculation [kg/s]	82.13	59.00	58.00	60.00	59.00
Carbonator flue gas recirculation [kg/s]	0.0	0.0	28.90	52.09	85
Make-up flow [kg/s]	11.15	8.36	5.57	3.34	2.00
Calciner thermal power [MW]	277	208	186	177	165
Carbonator cooling [MW]	58	51	34	31	30
Heat extracted from carbonator backpass [MW]	54	37	35	38	39
Heat extracted from calciner backpass [MW]	142	102	106	98	89

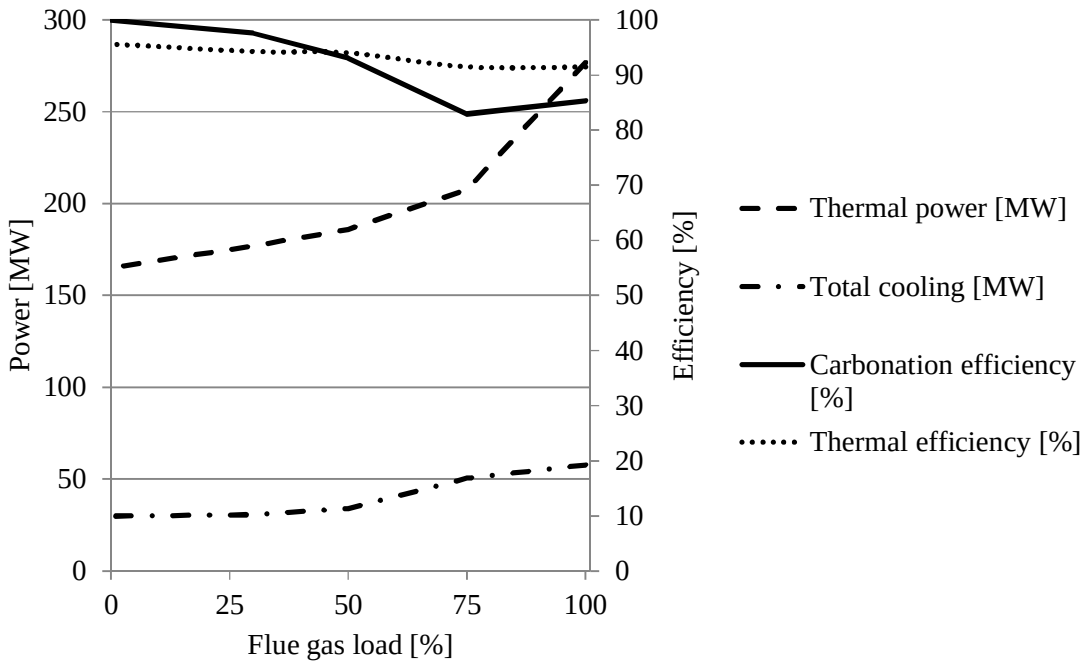

Figure 7. Thermal power of the calciner and total cooling of the carbonator plotted as a function of the flue gas load on the left hand side axis. In the same figure, carbonation efficiency and thermal efficiency of the calcium loop are plotted as a function of flue gas load (right hand axis).

The development of the flue gas recirculation is presented in Figure 8. Below the 75 % load the calciner flue gas recirculation is almost constant. In the carbonator the fuel gas recirculation increases linearly as the load is decreased until in the zero load scenario the whole reactor is fluidized with air. In addition to that, Figure 8 plots the average gas velocities in the reactors (left axis). The objective was to keep fluidization velocities constant in the reactors beyond 75 % load and use the solid material recirculation to adjust the flow of solids required for the CO_2 capture.

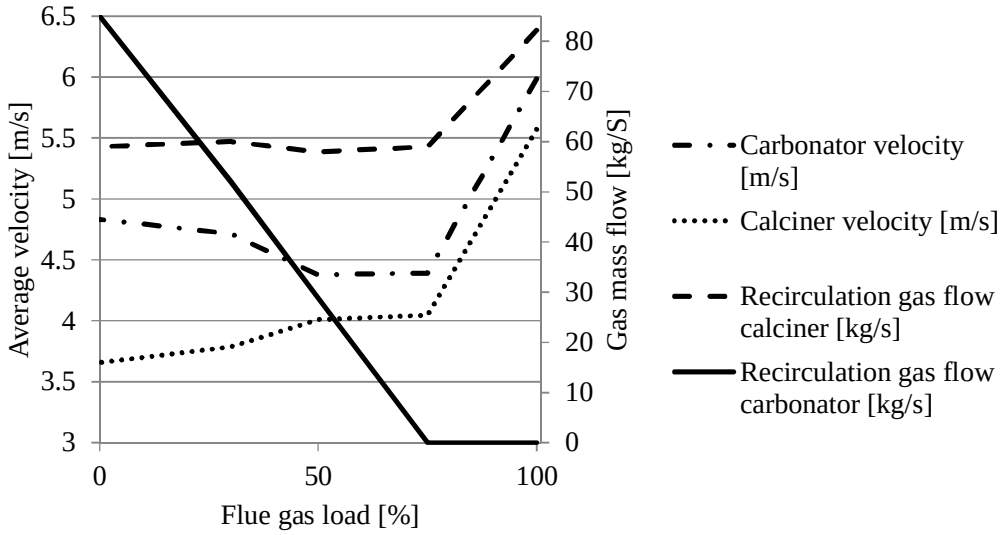

Figure 8. Recirculation gas flow to reactors in different load scenarios (right hand axis). Left hand axis presents the average velocity of the reactor in different load scenarios. Keeping average gas velocity close to the desired value becomes difficult in low flue gas loads.

However, maintaining gas velocities constant was not successful and the gas velocity drops in the calciner and increases in the carbonator due to the increase in the reactor temperature differences, Figure 9.

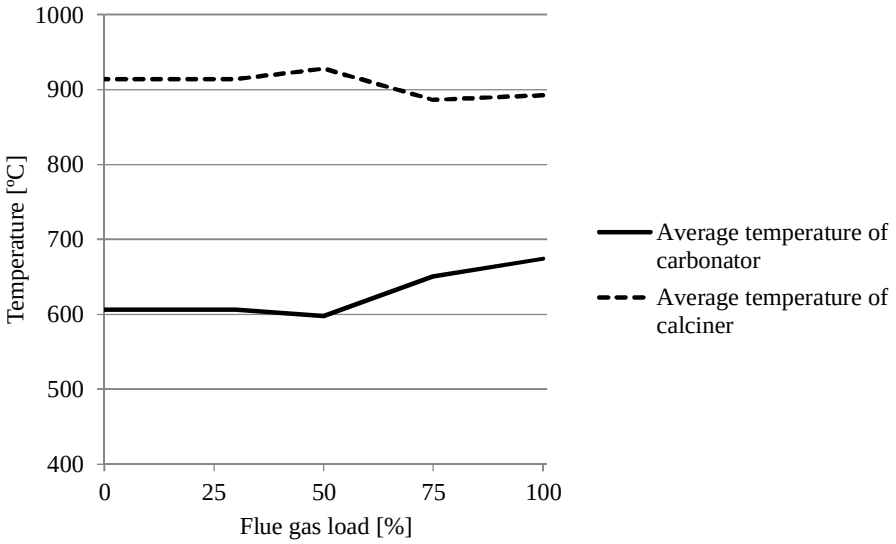

Figure 9. Average temperatures of the reactors in different loads. Several parameters affect the development temperatures in the reactors which in term have an effect on gas velocities. This creates a difficulty in controlling solid fluxes.

Figure 10 plots the adjustment of the make-up flow in different load scenarios and the control of solid flow between the reactors compared to the solid flow out of the carbonator. The make-up has been linearly controlled but it has a theoretical minimum set by the fuel ash and sulphur content. In the zero load case, the make-up

flow does not have any significance for the CO_2 capture, but it is needed to compensate the purge needed for the ash and $CaSO_4$ removal. In the same plot the solid flow out of the carbonator is presented alongside the solid flow lead from carbonator to the calciner. Several factors affect the solid flow out of the carbonator. Below the 75 % load, the attempt was to keep the gas velocity at around 4 m/s although the temperature change increased the gas velocity. This did not increase the solid flow because the carbonate content of the solids and the inventory of the carbonator decrease in the lower loads resulting in lower solid flows. The solid flow from the carbonator to the calciner was adjusted with solid recirculation and the percentage of recirculation had to be controlled case by case because the solid circulation rate out of the reactors is changing as a function of solid inventory and fluidizing velocity.

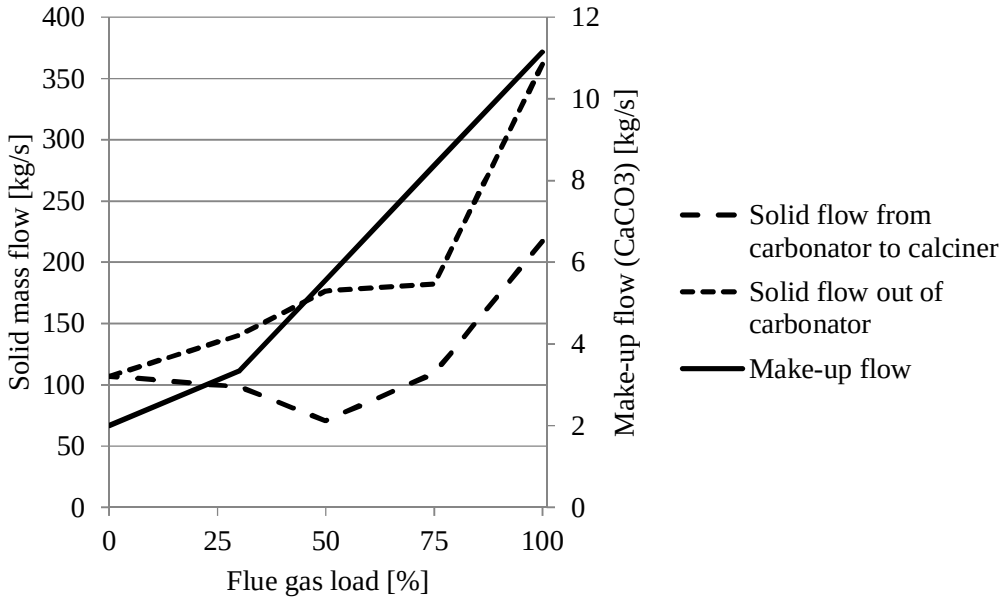

Figure 10. Solid flow out of the carbonator and solid allowed to the carbonator plotted as a function of flue gas load (left hand side axis). The solid mass flow has a lot of variation because it is dependent on several variables like gas velocity and reactor solid inventory and inventory composition.

An interesting observation is that in the zero load situation, fluidizing the carbonator with ambient air and running the calciner as an oxy-combustion circulating fluidized bed unit is also possible. Minimal heat was extracted from the external heat exchanger and solid train surfaces and the rest can be extracted in the backpasses of the reactors. If the power plant is abruptly shut down, the calcium loop can provide back-up power for extended periods.

To summarize the different load scenario analysis, flexibility can be achieved using solid and flue gas recirculation and clever heat transfer design. The flue gas flow out of the calciner in the zero load case drops to 60% of the full load flow which will certainly have an effect on the backpass heat exchanger performance. The thermal

efficiency in the partial loads will not be as good as predicted by the simplified approach used in this study. Also the performance of the turbulent bed external heat exchanger in lower loads is something that needs further investigation. Even if the flue gas load does not significantly change, several factors can affect the fluidization behavior of the calcium looping unit. The particle population of the system can change in size or density during the runs due to agglomeration or attrition which requires a change in fluidization. Because the calcium looping process is sensitive to the solid circulation rates between the reactors, effective ways to control solid circulation are necessary. Even though there might be some error in the prediction of solid circulation rates and heat transfer, the general observations from the simulations are applicable to the operation of large scale calcium looping units.

4 Conclusions

An existing 1-D dynamic calcium looping model was applied to a large scale calcium looping concept capturing CO2 from a 250 MWt power plant. Several new features were added to the model frame in order to successfully simulate the large scale unit, including new material fractions, ash and CaSO4, sulfur capture modeling and heat transfer in the solid return system. The plant was dimensioned based on the experience from large CFB units and the heat transfer design was evaluated based on the initial simulations of the design case. The unit was then simulated in five load scenarios ranging from full load to no flue gas flow to the carbonator. The results from the simulations confirmed that the successful operation of a large scale calcium looping unit requires good heat transfer design including the cooling of the hot solids coming from the calciner. Also the recirculation of flue gas in both reactors is necessary to ensure sufficient fluidization for different particle sizes or flue gas flows from the source combustor. Solid circulation control is also critical because it affects heavily the thermal balance of the system as well as the capture efficiency and CO2 balance. It was also observed that in the zero load situation fluidizing the carbonator with ambient air and running the calciner as an oxy-combustion circulating fluidized bed unit is also possible. If the power plant is abruptly shut down, the calcium loop can provide back-up power for some period. Utilizing the experience gained from large CFB-units coupled with new innovations, the scale-up of this process could be feasible in the near future. Further investigation of the solid mixing and temperature gradients in the carbonator and calciner bottom bed area with more detailed models like 3-D and CFD would confirm whether the capture efficiencies are as good as the 1-D model predicts.

References

Gonzáles, B., Alonso, M., and Abanades, J.C. (2010). Sorbent attrition in a carbonation/calcination pilot plant for capturing CO2 from flue gases. *Fuel*, 89, pp. 2918-2924.

Martínez, I., Grasa, G., Murillo, R., Arias, B., and Abanades, J.C. (2013a). Modelling the continuous calcination of CaCO3 in a Ca-looping system. *Chemical Engineering Journal*, 215-216, pp. 174-181.

Shimizu, T., Hirama, T., Hosoda, H., Kitano, K., Inagaki, M., and Tejima, K. (1999). A twin fluid-bed reactor for removal of CO2 from combustion processes. *Trans IChemE*, 77, pp. 62-68.

Ylätalo, J., Ritvanen, J., Tynjälä, T., and Hyppänen, T. (2014). Model based scale-up study of the calcium looping process. *Fuel*, 115, pp. 329-337.