



Advanced Indirectly Heated Carbonate Looping Process

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Deliverable D3.5:

Development of a two-stage calciner

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Author(s): Kyra Böge, Prof. Jürgen Karl

Affiliation: Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU)



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List of nomenclatures and abbreviations

CaCO_3	Calcium carbonate
CaO	Calcium oxide
CO_2	Carbon dioxide
MgCO_3	Magnesium carbonate
SiO_2	Silicon dioxide
Al_2O_3	Aluminium oxide
Fe_2O_3	Iron(III) oxide
MDK	Model Development Kit
XRF	X-ray fluorescence spectroscopy

List of symbols

n_{CO_2}	[mol/s]	CO ₂ released by reaction
$n_{\text{fluidisation media}}$	[mol/s]	amount of inert fluidization media
$p_{\text{CO}_2, \text{reactor outlet}}$	[bar]	CO ₂ partial pressure at the reactor outlet
p_{total}	[bar]	Pressure total

1 Introduction

The indirectly heated carbonate looping process separates the combustion from the calcination reaction. The heat is transferred by means of heat pipes. For efficient heat transfer, the two reactors are designed as fluidized beds.

Within the calciner, the critical objective is to effectively isolate pure CO₂ at the outlet of the reactor. This requires fluidization with CO₂. N₂ fluidization leads to N₂ being contained in the exhaust gas flow and CO₂ no longer being present in pure form. But if fluidization is carried by CO₂ then this leads to high calcination temperatures, agglomeration, and sintering. An alternative is calcination with steam. One approach is to calcine the limestone with CO₂ in the first reactor and the partially converted CaCO₃ enters a second reactor. The “second-stage calciner”, which is fluidized with steam due to which the residual conversion is achieved at lower temperatures. The aim here is not to supply any further heat to the reactor. This type of process control is intended to achieve energy savings in the first calciner. Within the scope of the deliverables, it should first be illuminated which energy savings can be achieved in the first calciner so that enough steam can be heated for fluidization with the residual heat. In the course of the project work, the solid/solid heat exchanger¹ established itself as an important component of the carbonate looping process as an alternative to the second-stage calciner. Based on the results, further interconnection variants were examined within the scope of this deliverable. The second aspect was the experimental investigations. A set-up for investigating the behaviour of the particles under the second-stage calciner conditions is to be examined.

In the course of the work on the deliverable, it became apparent that direct steam calcination plays an important aspect. In addition to the experiments on second-stage calcination, tests were carried out on direct steam calcination. With two different materials and a total of three different particle sizes. With the help of the experimental results and theoretical calculations, a recommendation is made for a process variant and the implementation of steam in the carbonate looping process.

¹ s. Deliverable 1.1 and 3.4

2 Methods

2.1 Theoretically

2.1.1 IPSE

IPSE is a software for heat and mass balance calculations and process simulations. It offers flexibility by allowing users to create and customize models. It excels in heat balance calculations and process simulations. IPSE's Model Development Kit (MDK) provides unique adaptability for creating new models and libraries. This software is being utilized to calculate the plant's economics by determining the optimal composition of the fluidized gas within the calciner. In contrast to other software programs, users are not confined to predefined models and model libraries by IPSE. While pre-made model libraries are available, they can also be customized to fulfill particular requirements. Thus, customizations were made in the pre-existing model using MDK to build a calciner and other component models for the process.

2.2 Experimentally

2.2.1 Used material

Table 1 Material properties of limestone from Messinghausen

production plant:	Messinghausen		
chemical characteristics:			
XRF	Mass.-%		
CaCO ₃	98,2		
MgCO ₃	1,2		
SiO ₂	0,4		
traces	<0,2		
physical characteristics:			
product:	0,1 - 0,315 mm	product:	0,3 - 0,7 mm
sieving, mm	fraction, Mass.-%	sieving, mm	fraction, Mass.-%
<0,100	14,6	0,315	9,4
0,100 - 0,125	12,4	0,315 - 0,400	10,3
0,125 - 0,160	17,5	0,400 - 0,500	26,7
0,160 - 0,2000	17,1	0,500 - 0,630	32,5
0,200 - 0,2500	15,3	0,630 - 0,710	12,4
0,250 - 0,315	14,7	> 0,710	8,7
0,315 - 0,400	8,2		
0,400 - 0,500	0,2		
> 0,500	0		

Table 2 Material properties of limestone from Istein

product:	0,2 - 0,5 mm
production plant:	Istein
chemical characteristics:	
XRF	Mass.-%
CaCO ₃	98
MgO	0,6
SiO ₂	0,7
Al ₂ O ₃	0,4
Fe ₂ O ₃	0,3
physical characteristics:	
sieving, mm	fraction, Mass.-%
>1	9,4
0,05 - 1,0	25
0,2 - 0,5	75
<0,2	5

2.2.2 Batch Calciner

The batch calciner is known from the CARINA project and has not been in use since 2016. Before the commissioning, electrical heating elements had to be exchanged, thermocouples were installed, and an exhaust gas cleaning was installed. Figure 1 showing the picture of the CAD drawing, calciner, control system, and observation window. The batch calciner has a total power of 18.2 kW with an additional gas preheating of 4 kW. The fluidization medium is changeable and can be set between 1 and 15 Nm³·h⁻¹. The reactor content is between 15 and 25 kg. The batch calciner consists of three different heating zones, which can be observed and controlled separately. The fluidized bed lays on three weight cells so that the weight changes during calcination and carbonation can be observed. On the top of the calciner, there is an observation window for observing the fluidization of the sample. In Figure 1, there is a picture of a limestone sample during self-fluidization through CO₂ released from calcination. The red colour shows temperatures of around 900 °C. Figure 1 also shows a picture of the control system by B&R. The control system allows automated process control and recording (s. D. 1.5). For the steam experiments, a steam generator was added, the control system adapted, a nozzle implemented and a condensate trap set up.

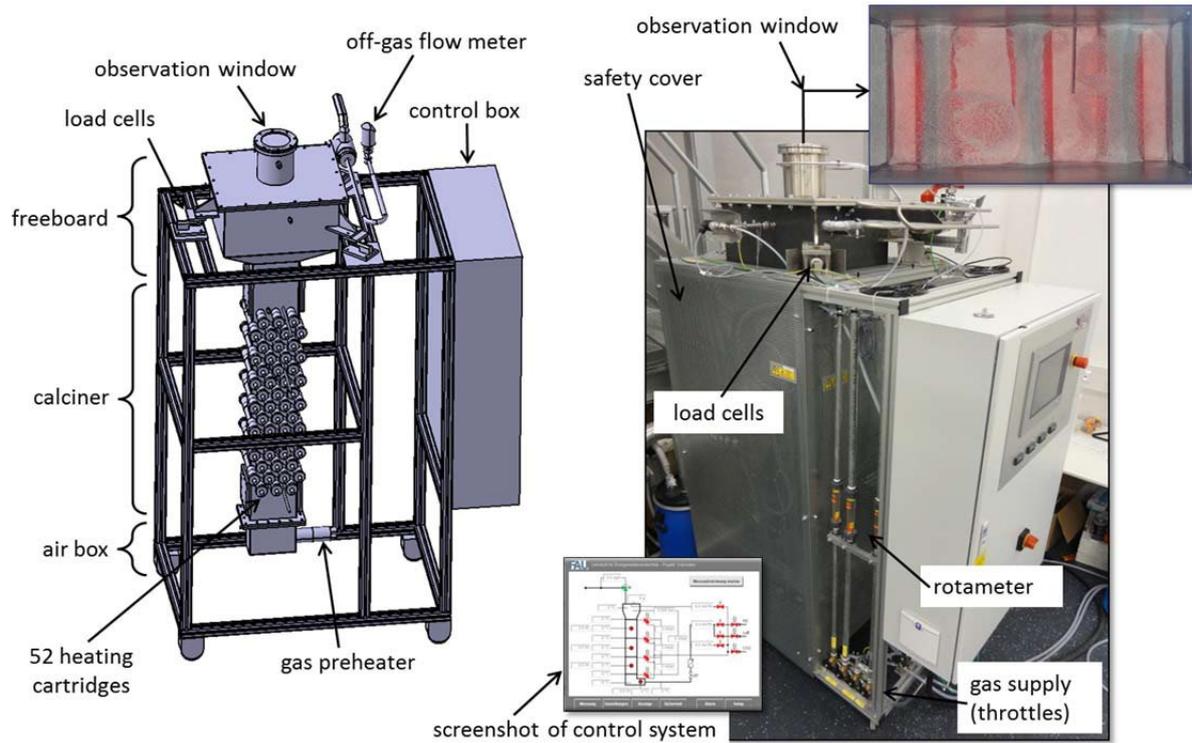


Figure 1: The batch calciner is a fluidized bed with 52 electrical heat pipes with a total power of 18.2 kW simulating the heat pipes of the scale-up plant (Hoeftberger 2016).

2.2.3 Small scale fluidized bed

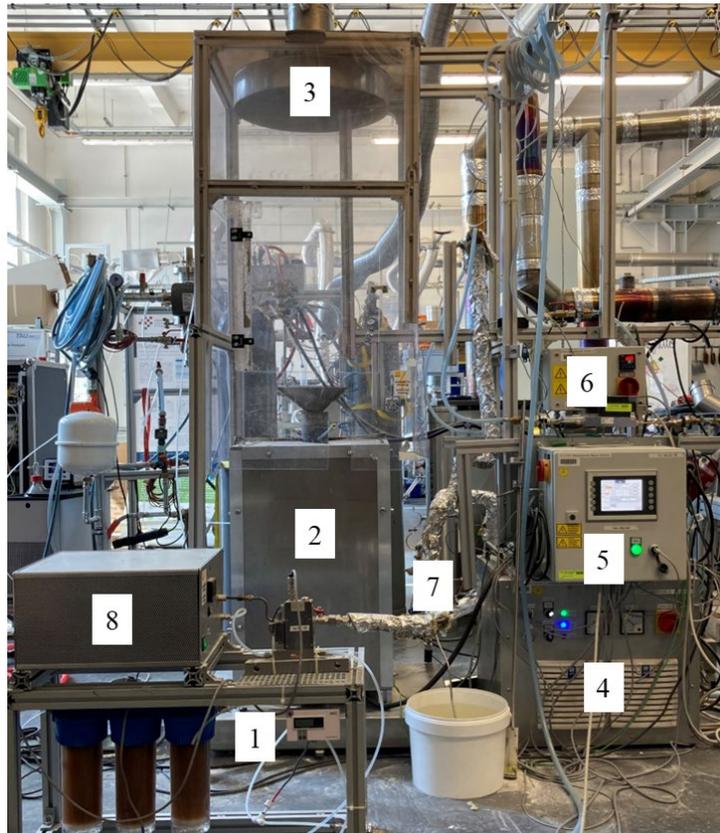


Figure 2: (1) shows a picture of the small scale fluidized bed with: balance (1), tube furnace fluidized bed (2), exhaust (3), electrical regulation (4), control system (5); control box gas preheating (6); gas preheating section (7); steam generator (8).

The fluidized bed consists of a tube reactor, which is surrounded by two heating shells with a total power of 4,6 kW which stands on a balance. The reactor can be operated with 1 - 8 Nm³/h medium of N₂/CO₂/H₂O. The gas is preheated before entering the reactor by means of a heating cord. A pressure sensor and a thermocouple are located in the gas preheating section. All components are controlled and regulated by the B&R system. The system also allows continuous data recording.

3 Results and Discussion

3.1 Heat demand

Theoretically, this work package will consider the extent to which a second-stage calciner proves to be energetically advantageous. In order to be able to evaluate this statement, the possible circuit variants must first be considered. First case: In this case, the sorbent is circulated between the calciner and the carbonator. Second case: An optimisation process; which is also a project task; is the use of the waste heat of the sorbent flow coming from the calciner to preheat the CaCO_3/CaO flow from the carbonator before it enters the calciner. For this purpose, a solid/solid heat exchanger is being designed in the project task 3.3. The energy saved in this case is to be simulated. Third case: It consist of the second-stage calciner and the heat saved by this. Fourth case: The further optimisation would be the coupling of solid/solid heat exchanger and second-stage calciner. Fifth case: The optimisation case, that is considered and will be worked out later experimentally, is the direct fluidization with steam. Sixth case: During direct calcination, residual heat remains, which can then be used again by a solid/solid heat exchanger. The connection variants are shown in Figures 3 and 4.

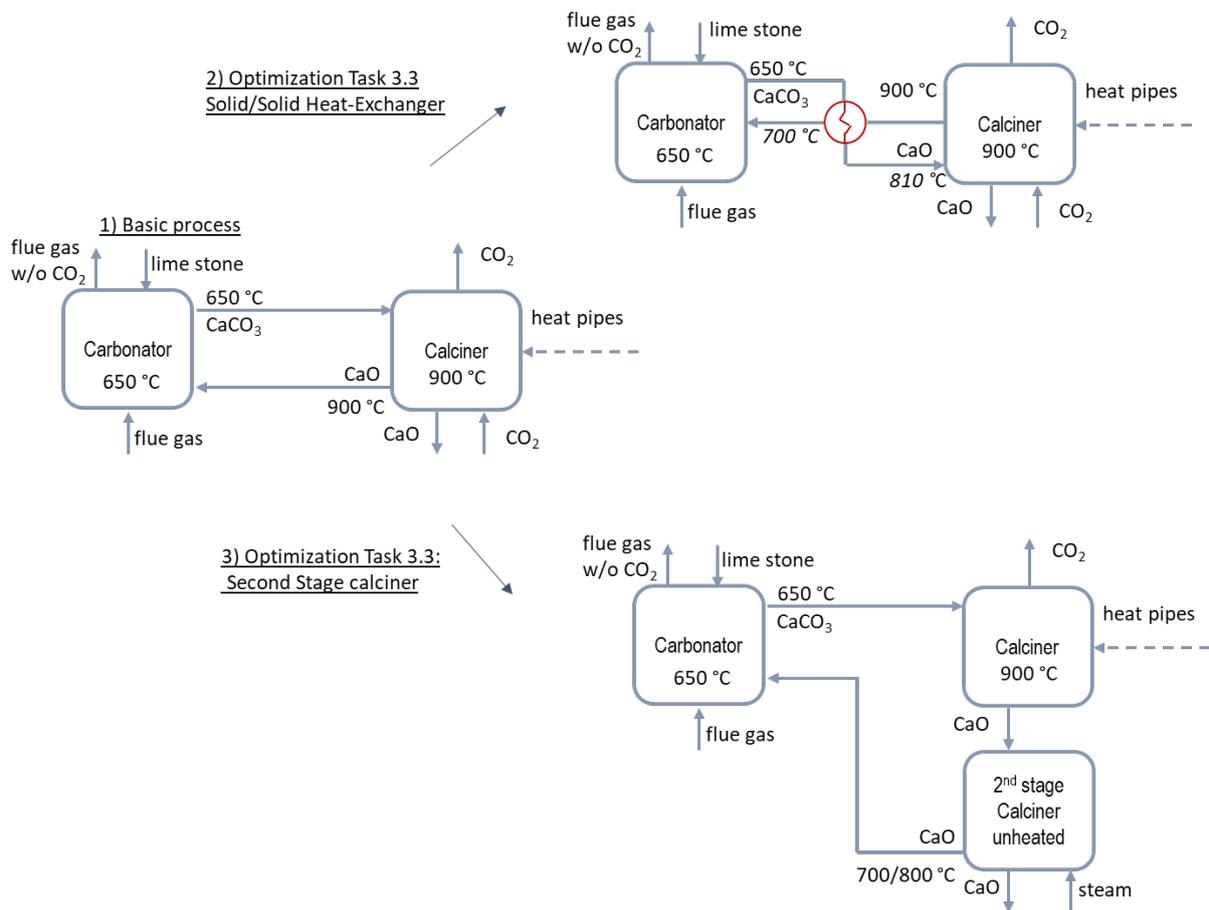
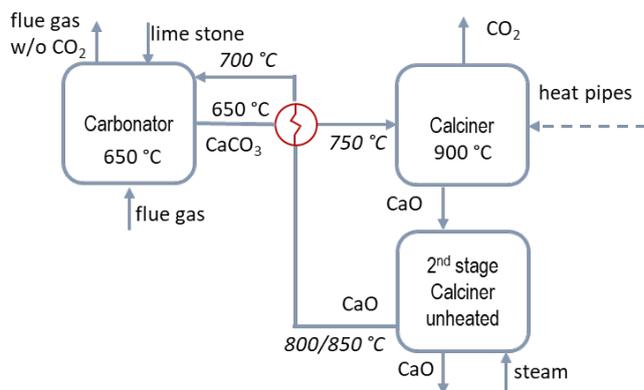
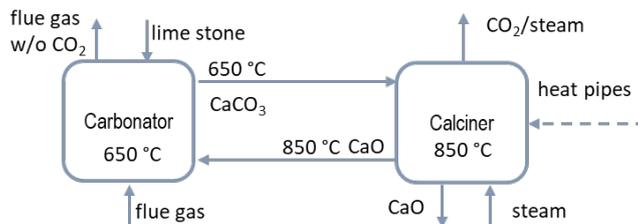


Figure 3: Schematic representation of the basic process and the two optimization approaches: Solid/Solid Heat-Exchangers and Second-Stage-Calciner.

4) Optimization: Combination solid/solid Heat Exchanger and Second Stage calciner



5) Optimization: Direct steam calcination



6) Optimization: Combination solid/solid Heat Exchanger and direct steam calcination

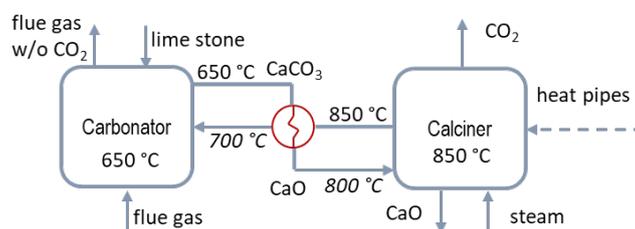


Figure 4: Schematic representation of the three further optimization cases

The table 3 shows the parameters that serves as input parameters for the respective cases. These were taken from Deliverable 1.1 and Deliverable 3.4.²

Table 3 Parameters for the IPSE calculation

	Case	Hellas						Hönnetal					
		1	2	3	4	5	6	1	2	3	4	5	6
Carbonator													
Operating temperature	°C	650						650					
Exhaust gas from IHCaL combustion	kmol/s	0,37						1,58					
Molar total CO ₂ content in flue gas	mol/mol	0,16						0,16					
Flue gas inlet temperature	°C	336						574					
Temperature of the sorbent at the carbonator inlet	°C	700						656					
Molar conversion of the sorbent leaving the carbonator	mol CaCO ₃ /mol CaO	0,142						0,154					
Carbonator Efficiency	%	0,9						0,9					
calciner													
Operating temperature	°C	900			850			900			850		

² Deliverable 1.1 and 3.4 created within the ANICA project Carina Hofmann, Kyra Böge, Christos Papalexis, Myrto Zeneli, Nikos 2023; Martin Greco-Coppi (TUDA), Konstantina Peloriadi (CERTH 2022)

Table 4 Parameters for the IPSE calculation

Molar flow of the sorbent Inlet calciner	kmol/h	1427						5473					
Temperature of sorbent Inlet calciner	°C	650	810	650	760	650	760	650	810	650	760	650	760
Purge CaO flow	t/day	145						582					
Available heat flow from combustion	MW	15,73				16,44		59,22				62,23	
Molar conversion after first calciner	mol CaCO ₃ / mol CaO	1		0,95		1		1		0,95		1	
Heat exchanger													
Temperature of cold flow before heat exchanger (carbonator outlet temperature)	°C	650		650		650		650		650		650	
Temperature of cold flow after heat exchanger (Calciner inlet temperature)	°C	n.a		810		n.a		760		n.a		760	
Temperature of warm stream before heat exchanger (calciner outlet temperature)	°C	900		850		850		900		850		850	
Temperature of warm stream to HE	°C	699		712		712		695		710		710	
Combustion													
Operating temperature	°C	1000				950		1000				950	
Fuel mass flow	kg/s	0,81						5,27					

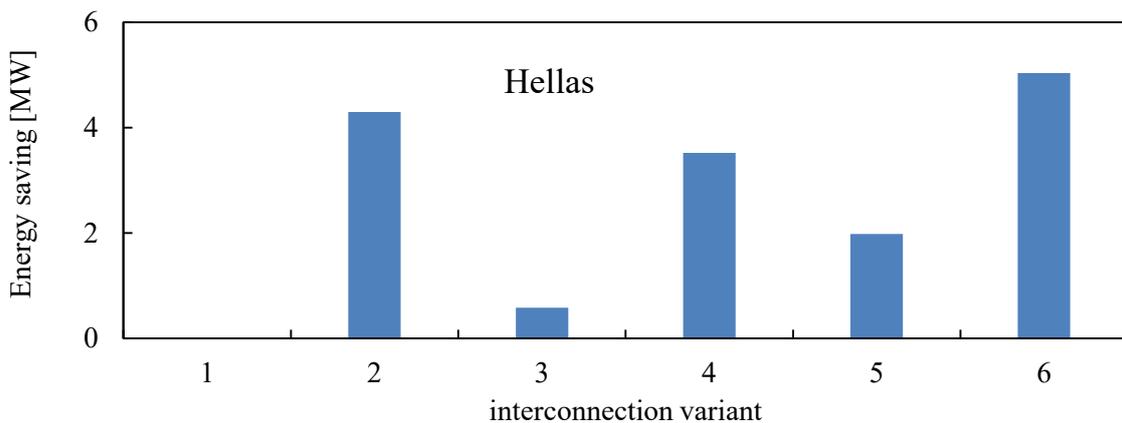


Figure 5 shows the energy savings of the optimization compared to the standard case for the lime plant used in the project, CaO-Hellas.

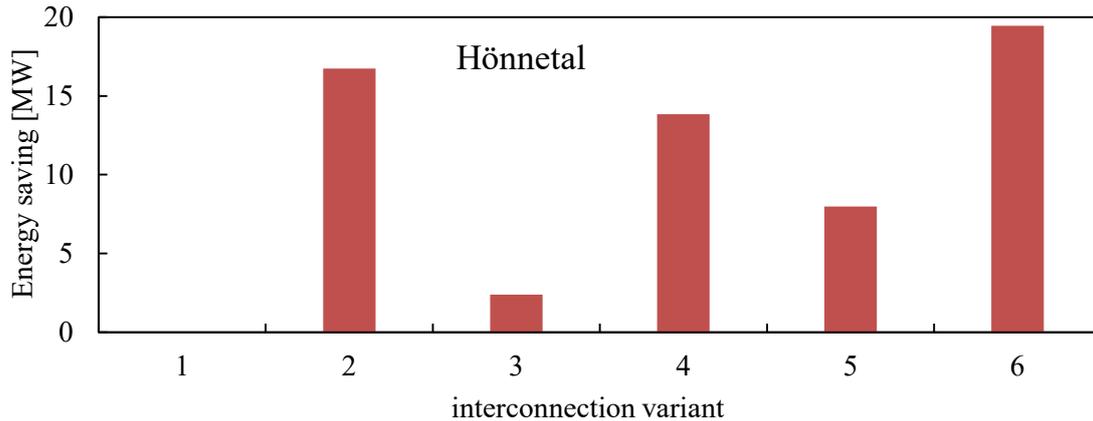


Figure 6 shows the energy savings of the optimization compared to the standard case for the lime plant used in the project, Hönnetal.

Figure 5 and Figure 6 show the results of the IPSE simulation. From the results of the simulation, it becomes clear that the greatest energy savings are available when a solid/solid heat exchanger is integrated into the looping-process and heat is recovered. A process with a second-stage calciner alone produces only a small saving for both systems. This is because the second-stage calciner is intended to operate without additional heat supply. The required steam must be preheated by the sorbent; as additional energy is required for additional steam supply. As will be shown in the following: this means that only very small amounts of conversion can be saved in the first calciner. The energy saving is low. Direct calcination (case 5) with steam would result in greater energy savings, although here, as in the case of CO₂ fluidization, the provision of the fluidising medium has not been taken into account. The greatest energy saving can be achieved with direct steam calcination and the subsequent use of the residual heat of the sorbent leaving the calciner to heat the return flow from the carbonator before entering the calciner.

3.2 Design diagram second stage calciner- case 3

The energy balances for the case of the second-stage calciner are shown below. To illustrate this, the amount of energy that can be saved for both plants is shown, depending on the conversion in the first calciner, as well as the energy that remains or is required to achieve the respective conversion. Figure 7 gives a detailed view of the saved turnover when 10 % still have to be converted. The diagram clarifies once again that the savings amount to only a negligible fraction in comparison to the entire reaction. The simple plot shows why the energy savings in case 3, i.e. the case of the second-stage calciner, are small. The energy required to

calcine 10 % is comparatively low. Gas preheating and circulated material heating account for the majority of the energy demand.

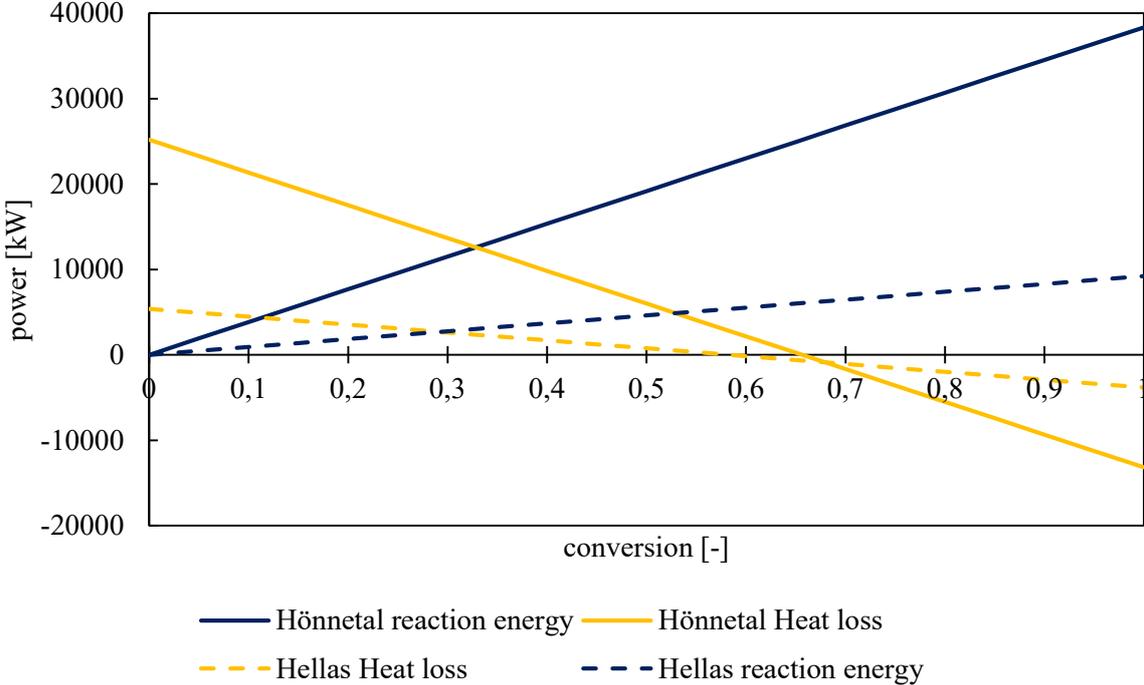


Figure 7 shows the energy (heat losses) that remains in each case as a function of the conversion for both demonstration systems. For illustration purposes, the reaction energy is also plotted as a function of the conversion.

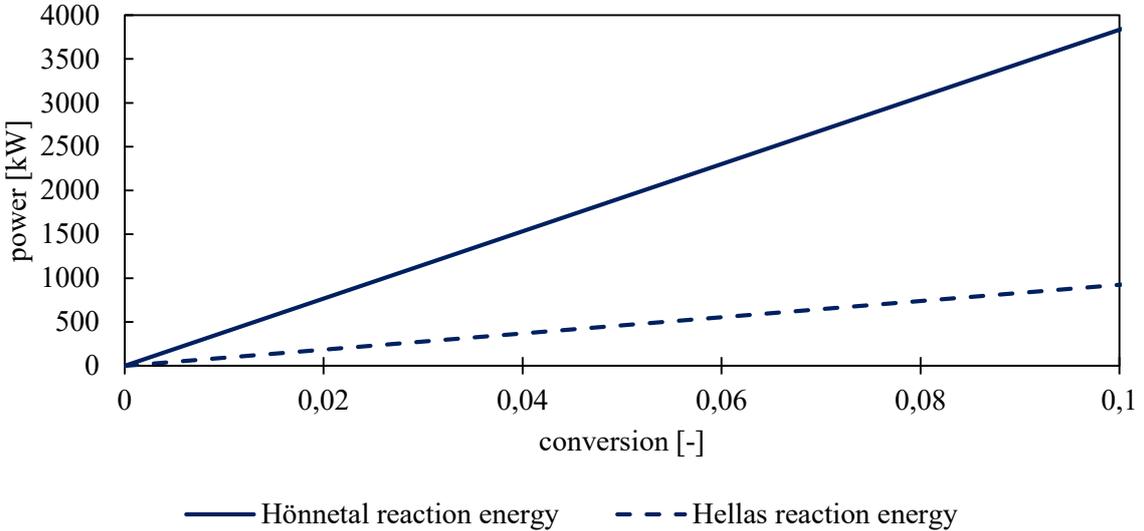


Figure 8 shows a detailed view of the reaction energy as a function of the conversion for both model plants.

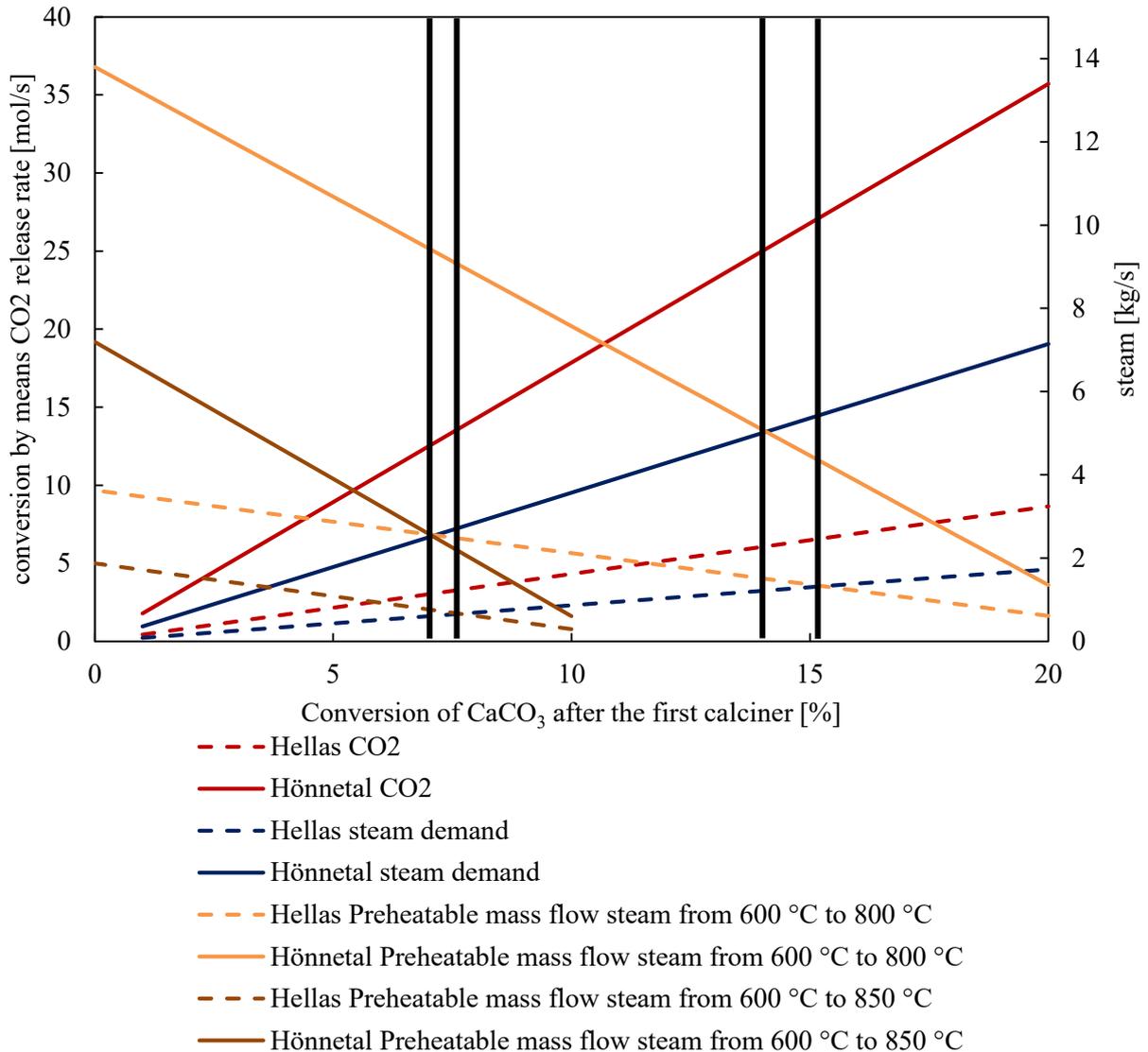


Figure 9 shows that the steam mass flow rate for the Hönnetal and CaO Hellas model plants is a function of the conversion without the steam cooling down the plant any further. Furthermore, the mole flow of CO₂ is shown and its dependent on the partial pressure. Equation 1 is used to calculate the steam demand, so that the partial pressure at the reactor outlet is set at the level of the equilibrium curve as determined experimentally. The turn-over point is shown in black, where more steam can be heated than is needed.

The following Figure 9 illustrates the discussion based on a residual turnover of 10 %. On the other hand, Figure 9 shows the required CO₂ release rate as a function of the conversion rate on the basis of the specified cycle (c. Table 1). Furthermore, the heatable mass flow of steam, which enters the second-stage calciner at 600 °C is shown at 800 °C and 850 °C degrees respectively. In the event that the steam is to be heated to 850 °C, a positive energy balance can only be achieved at all from 10 % residual conversion. For this reason, it was decided to continue calculating at 800 °C, since a significantly larger amount of steam can be heated. Based on the results from the batch-calciner, the partial pressure can be used to calculate the amount of steam required as a function of the CO₂ release. The turn-over point can be calculated from the diagram by plotting the steam requirement and the heatable mass flow till the point at which more steam can be heated than required.

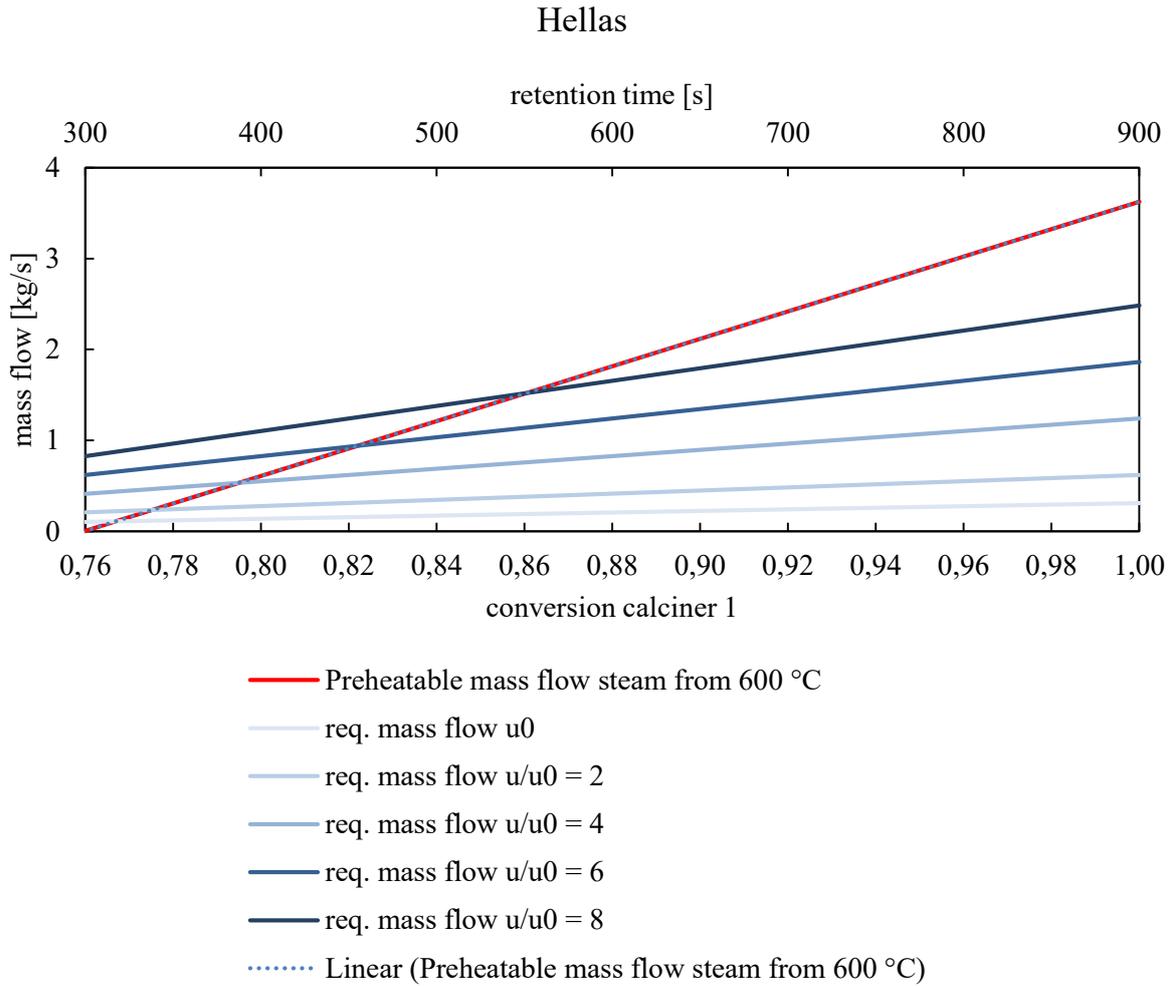


Figure 10: Design diagram for dimensioning the second-stage calciner in the lime plant Hellas for a limestone with Sauter diameter 0.6 mm. In red, the course of the preheatable steam entering the second-stage calciner at 600 °C is shown, depending on the conversion in the first calciner. The mass flows required for fluidization are shown in blue, depending on the desired mode of operation. The retention times result for a reactor height of 2m.

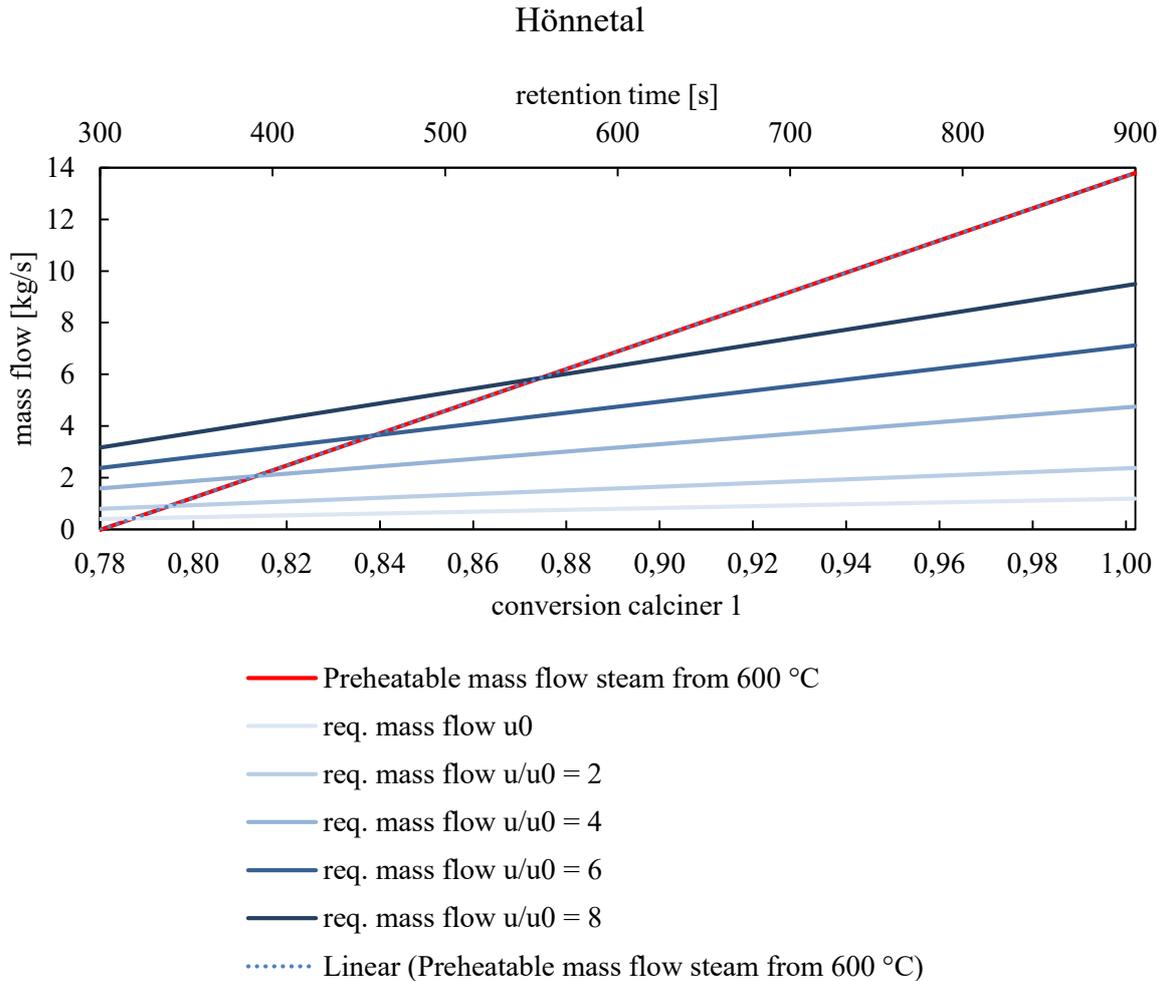


Figure 11: Design diagram for dimensioning the second-stage calciner in the lime plant Hönnetal for a limestone with sauter diameter 0.6 mm. In red, the course of the preheatable steam entering the second-stage calciner at 600 °C is shown, depending on the conversion in the first calciner. The mass flows required for fluidization are shown in blue, depending on the desired mode of operation. The retention times result for a reactor height of 2m.

The design diagrams were drawn up for both plants. On the one hand, it is to be shown which conversion can be saved in the first calciner so that the fluidization medium steam with an inlet temperature of 600 °C can be preheated to the reaction temperature 800 °C for the second calciner. The design diagram also shows which mass flow of steam is required depending on fluidization u/u_0 and residence time (i.e. reactor size). It shows that in the Hellas case, a minimum conversion of 0.76 must be achieved in the first calciner, and 0.78 in the Hönnetal case. If less conversion is achieved, the sorbent stream exiting the first calciner would not have enough heat so that reaction can still take place and the steam can be heated from 600 °C to 800 °C. The area between the red line, which represents the heatable steam mass flow, and the blue line of steam demand for a fluidization of $u/u_0 = 8$, represents the area of excess energy of the outgoing CaO flow from the calciner or second-stage calciner.

Considering Figure 9 and the turn-over point, the first calciner in the Hellas case must achieve 15 % turnover, 1.5 kg/s are still required for the remaining turnover. For the Hönnetal case, it must achieve 14% turnover but 5.1 kg/s are still required for the remaining conversion. With the help of the design diagram, it is possible to define which retention time and fluidization are set when the second-stage calciner is designed as a fluidized bed. If less conversion were to

take place in the second calciner, unused energy would remain. In general, it should be noted that no energy losses have been taken into account so far.

In summary, it can be seen that the greatest energy saving is achieved by a solid/solid heat exchanger. By implementing a second-stage calciner, the energy required to preheat the input stream to the calciner through a solid/solid heat exchanger would be removed. The calculations and design diagrams also show that the energy savings of a second-stage calciner are low, as it can only be used sensibly from a residual conversion of 15 % in the Hellas case and 14 % in the Hönnetal case. However, there is a need to use steam because of the direct steam calcination. Coupling this with the solid/solid Heat Exchanger results in the greatest savings.

3.3 Experimentally

Due to the theoretical consideration and the potential of the greatest energy saving through direct steam calcination, it is necessary to consider the case. In the first step, batch experiments were carried out. In a third series of experiments, the case of the second-stage calciner, as described in the project proposal, was simulated. For this purpose, a second reactor was operated, in which samples could be better added and removed. The second-stage calciner was first fluidized with CO₂ and then with steam.

3.3.1 Batch experiments

Due to the theoretical consideration and the potential of the greatest energy saving through direct steam calcination, it is necessary to consider the case of direct steam calcination. For this purpose, experiments were carried out with two particle fractions 100-300 µm and 300-600 µm of the limestone from the production plant Messinghausen and 200-500 µm from the production plant Istein under H₂O / N₂ / CO₂ atmosphere at different temperatures. The weight loss of the CO₂ released was determined by means of load cells, which made it possible to calculate the conversion and the partial pressure at the reactor outlet.

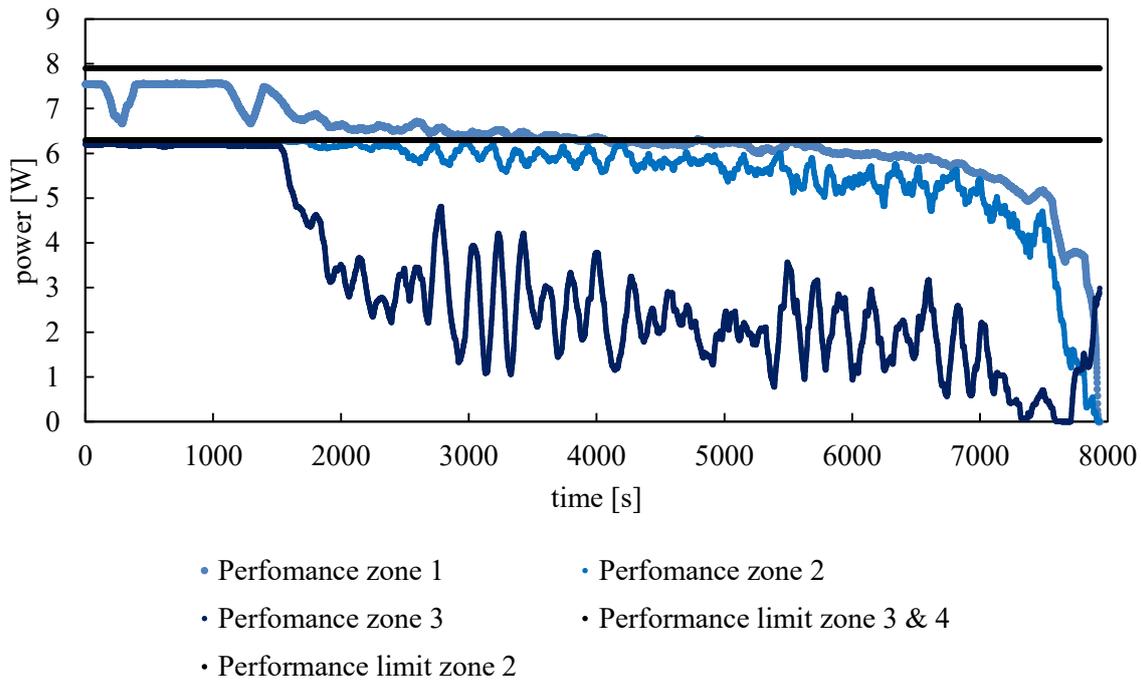


Figure 12 shows the power diagram of the three heating zones of the reactor and in black the power limit of the respective heating zones.

Figure 12 shows representatively the course of the power build-up of the three different zones in the calciner batch. At the start of the heating phase, the reactor operated at its power limit due to the ongoing heating process and the ongoing reaction until it reached the target temperature of 840 °C. As soon as the target temperature is reached, the existing heating capacity of the reactor is sufficient. The reaction is therefore not limited by the heat input.

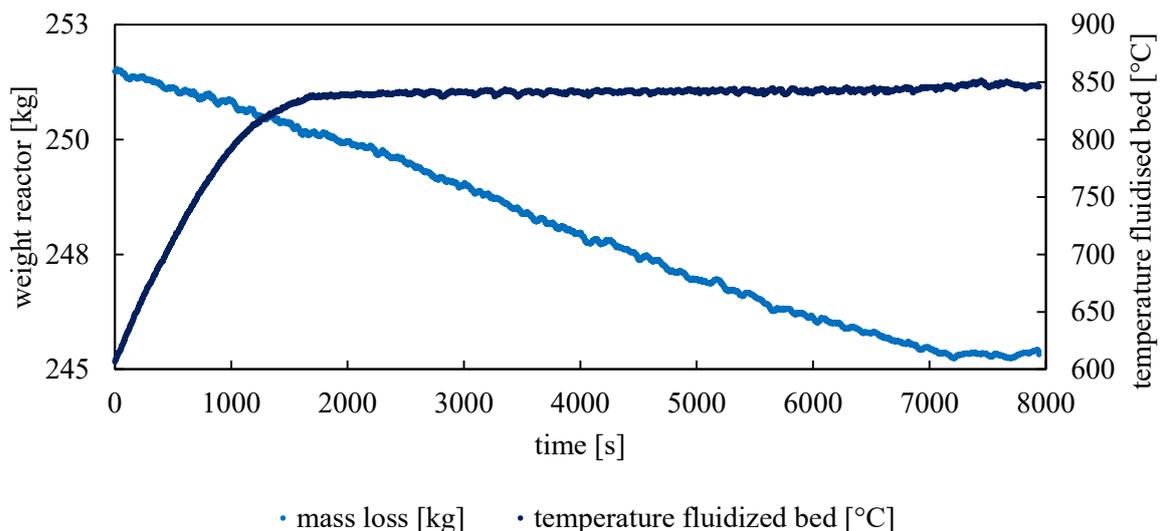


Figure 13 shows for a batch test at a target temperature of 840 °C with fluidization of 0.077 mol with of the fluidized bed temperature and the moving average over 50 measuring points of the measured weight curve over time and the fluidized bed temperature.

Figure 13 shows the temperature curve of the fluidized bed and the weight reduction over time. The reaction already starts during the heating process. This cannot be prevented in batch tests.

The reactor could be purged with CO₂ beforehand to prevent the reaction from starting, but the CO₂ that is in the reactor would hinder the start of the reaction. At 850 °C, at least a partial pressure of 0.5 bar must be reached. Therefore, it cannot be ruled out that the reaction starts unlimited.

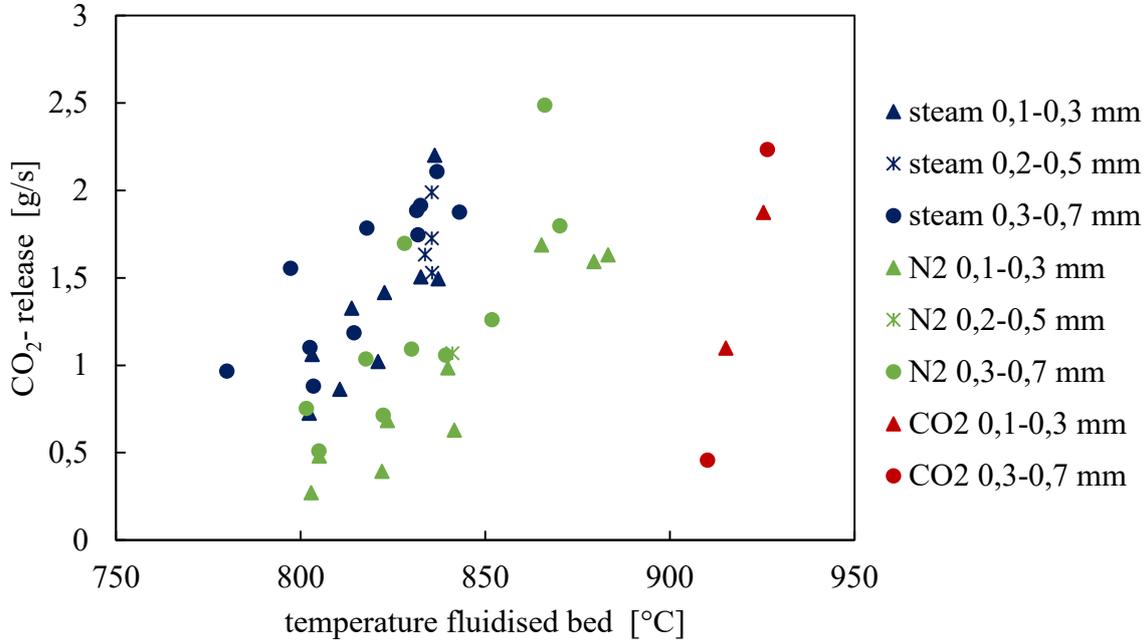


Figure 14 shows the reaction time in batch calciner tests with reactor initial mass of 15 kg CaCO₃ with different fluidization and temperature. The bubble size represents the fluidization in each case.

In Figure 14, the CO₂-release rate is plotted against time, for the three materials used and the three fluidization media H₂O / N₂ / CO₂. It shows that steam at lower temperatures has the same release rate as N₂ at higher temperatures. Furthermore, it can be seen that significantly higher temperatures are required for CO₂ in order to obtain the same CO₂ release rates. In addition, it can be seen that the proposed 900 °C for calcination under 100 % CO₂ conditions is not sufficient in terms of temperature and that higher temperatures are necessary for significant release rates. Furthermore, a trend can be seen, contrary to expectations small particles have smaller release rates under H₂O and N₂ atmospheres than the larger particle fraction.

In the next step, the experiments depicted in Figure 14 were plotted using the partial pressure at the reactor outlet, which was calculated based on the weight measurement and the set fluidization conditions. For calculating the partial pressure, following equation is used which is shown below. For better comprehension, the calculation of partial pressure is depicted using molar flows, highlighting that the quantity of fluidization, as explained in the following diagram, has a substantial impact on the reaction rate.

$$p_{CO_2, reactor outlet} = \frac{n_{CO_2} [\frac{mol}{s}]}{(n_{fluidization media} [\frac{mol}{s}] + n_{CO_2} [\frac{mol}{s}])} * p_{total} \quad \text{eq. 1}$$

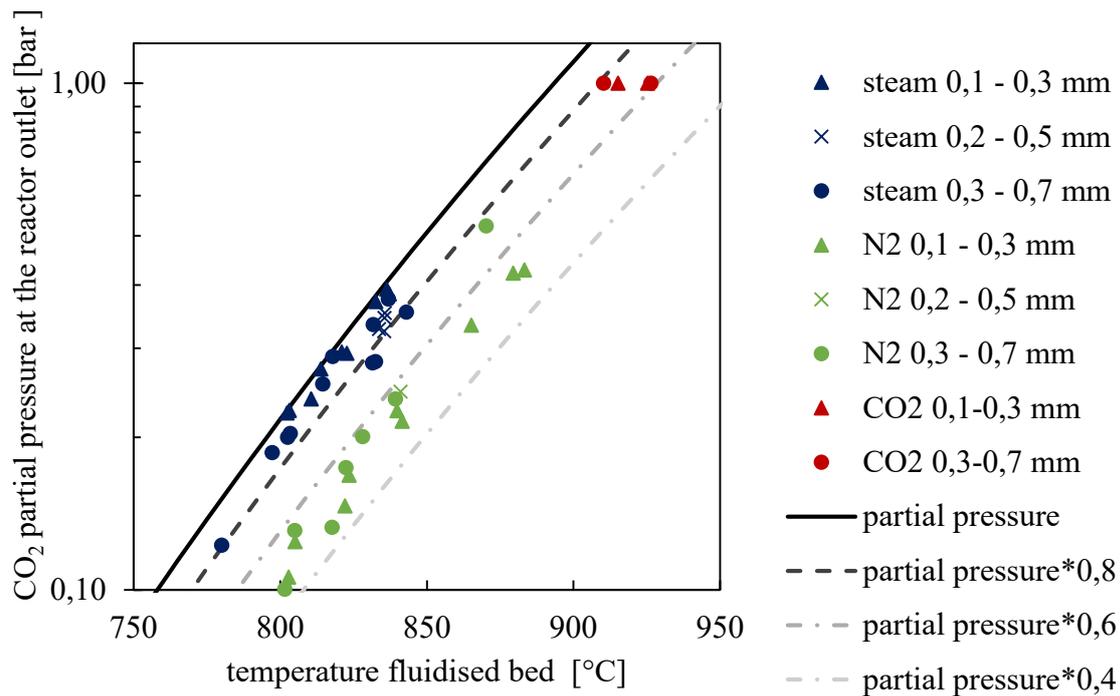


Figure 15 shows the calculated partial pressure at the reactor outlet of the respective tests from Figure 14.

This application, which is generally applicable and independent of reactor-specific parameters, can explain the observations presented in Figure 11. It can be observed that regardless of the fluidization conditions, the partial pressure at the reactor outlet at the respective temperature aligns closely with the equilibrium line for steam experiments and deviates by approximately 10% and for nitrogen experiments by 50%. This also makes it clear that experiments with low fluidization needs a longer time, since the reaction rate is determined by the partial pressure at the reactor outlet. Furthermore, it shows that with steam, a significantly higher partial pressure can be achieved at the reactor outlet than with N₂, which also explains why experiments with steam run significantly faster. The observations are in line with the literature where steam is said to have a catalytic effect (Wang et al. 2008; Silakhori et al. 2021). From the observations it is clear that there is a g/s dependent CO₂-release rate. This is confirmed and illustrated by the following experiments. Four experiments were carried out under the same fluidization conditions with different weights.

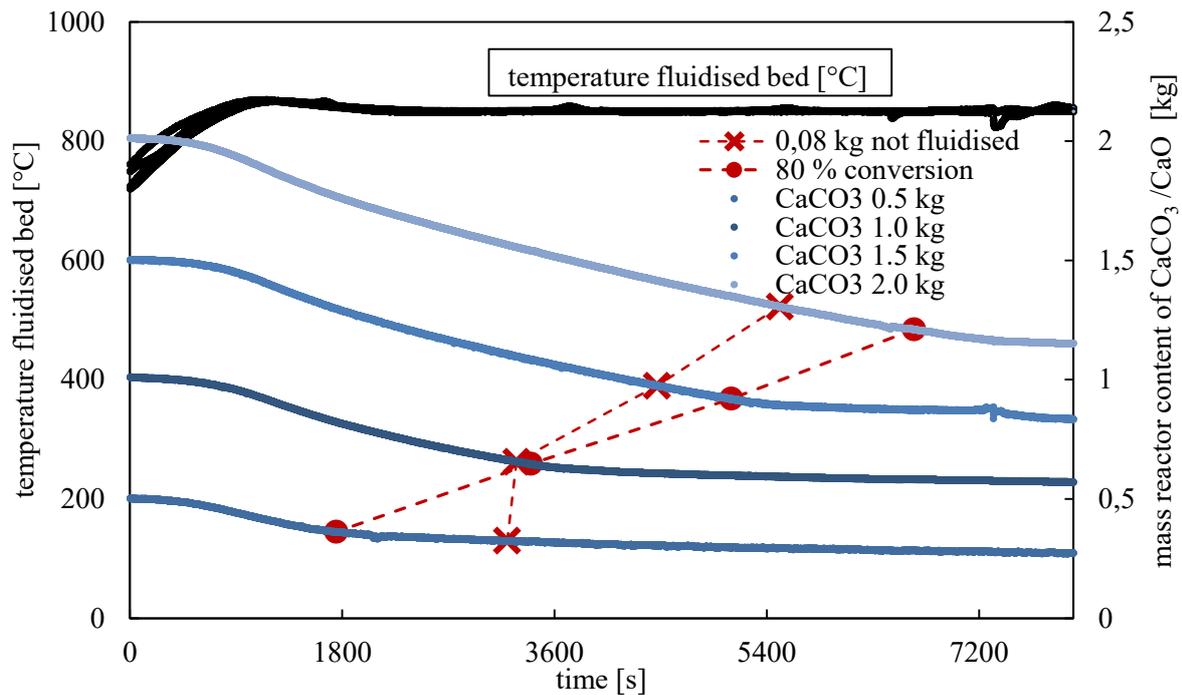


Figure 16 shows the weight course of calcination under the same experimental conditions $T = 850\text{ }^{\circ}\text{C}$, fluidization N_2 with $u/u_0 = 4$ over the time of four experiments with different reactor contents CaCO_3 with starting mass 0.5/ 1/ 1.5/ 2 kg and the fluidized bed temperature of all four experiments. Marked is the range • with 80 % conversion and x conversion minus a reactor content 0.08 kg.

It is clear that experiments with twice the reactor capacity take twice as long to reach 80 % conversion. The experiments were carried out in the small scale fluidized bed.

3.3.2 Second-stage experiments

In a further step, semi-batch experiments were conducted that precisely replicate the application of the second-stage calciner. The reactor was preheated to $920\text{ }^{\circ}\text{C}$ with approximately 1 kg of CaO particles and fluidized with CO_2 . A 100 g sample of CaCO_3 particles was preheated and added to $600\text{ }^{\circ}\text{C}$. Initially, calcination takes place under a CO_2 atmosphere, and then at a certain conversion level (30/ 50/ 70/ 90 %), the fluidization is switched from CO_2 to steam, and no further heating is applied. In the case of adapting the batch calciner through a second-stage calciner, the particles would experience exactly this behavior.

Figure 17 shows the temperature curve during the experiments. First, calcination was carried out under a CO_2 atmosphere with further heating. Then it was switched to steam calcination and no further heating was added.

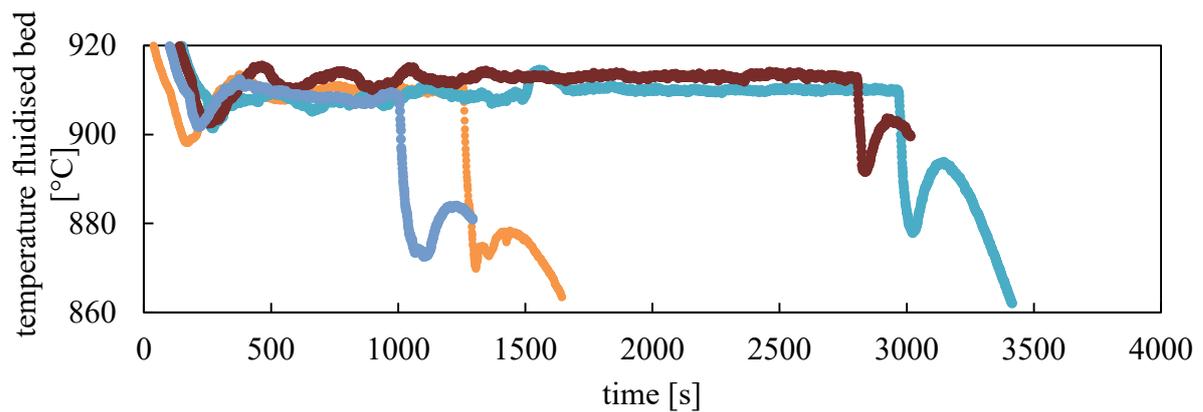


Figure 17 shows the temperature curve during the experiment, initially calcination was carried out at approx. 910-915 °C under CO₂ fluidization, until the system was switched over to steam fluidization at different rates and no further heating power was supplied to the reactor.

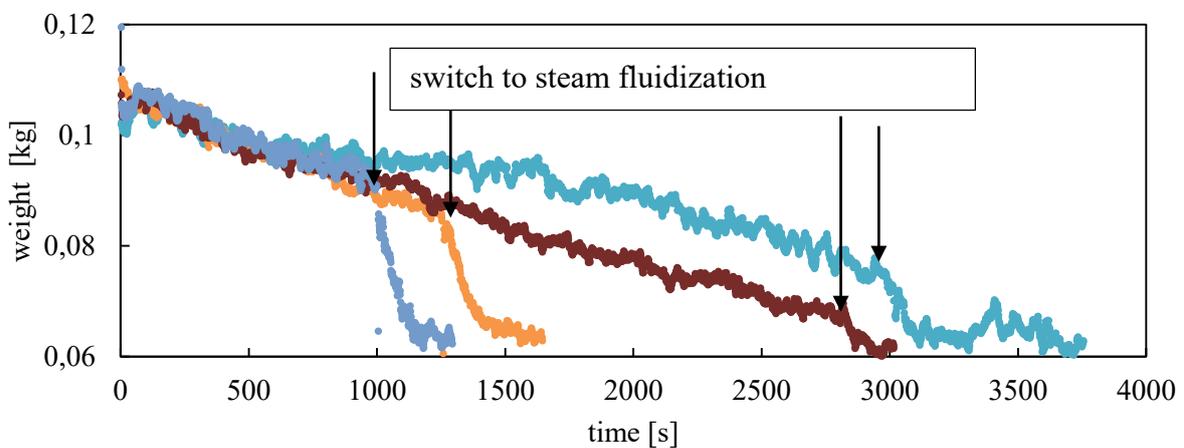


Figure 18 shows an example of the curve for the particle size 0.1-0.3 mm for the calcination of 100 g CaCO₃ under CO₂ atmospheres at 915 °C and switching to steam fluidization at different conversion (30/ 50/ 70/ 90 %), times and no further heating.

In Figure 18, the weight is plotted over time after introducing 100 g of CaCO₃ into the fluidized bed of calcined limestone (CaO). The arrows mark the time when the fluidization was switched from CO₂ to steam. It can be clearly seen that an accelerated CO₂ release takes place under steam atmosphere independent of the conversion progress.

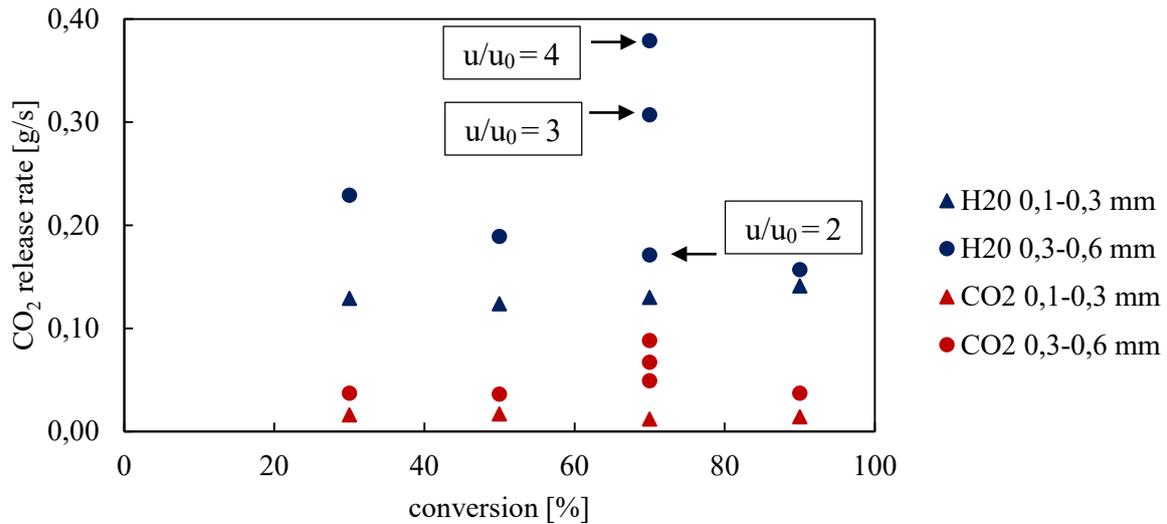


Figure 19 shows in red the release rate under CO₂ fluidization at 910 - 915 °C and in blue the release rate under steam atmosphere after switching from CO₂ to H₂O at different conversions and no further heating.

Figure 19 shows the release rates of the entire series of experiments for two materials. For all experiments, the first step was calcination with CO₂ and then, at a certain conversion rate (x-axis), the switch was made to H₂O fluidization. For the particle size 0.3-0.6 mm, the test was carried out three times with three different fluidization rates when switching over at 70 % conversion. It can be clearly seen that the CO₂ release rate is significantly higher under steam fluidization. It can also be seen that the release rate is higher for the particle size of 0.3-0.6 mm. This is due to the equilibrium-dependent reaction rate phenomenon described above. For larger particles, more steam is required for the same fluidization, which means that more CO₂ can be released at the same partial pressure. Furthermore, it can be seen that for the same particle size, CO₂ release under steam atmospheres is dependent on fluidization. This again confirms the theory of CO₂ release described above. The experiments again show the dependence of the CO₂ release rate on the fluidization medium. It can be shown that this also applies if calcination is previously carried out in the fluidized bed under CO₂ atmosphere. For the design of the fluidized bed, the equation of the partial pressure calculation can therefore always be used. The partial pressure is given by the set fluidized temperature. In the partial pressure calculation, the further degree of freedom is the amount of fluidization medium, which is also given as a process parameter, which then automatically results in the CO₂ release rate. Thus, the partial pressure calculation can always be used for the design of the fluidized bed calcination as shown in Figure 15. The tests also show that in the case of a retrofit of a second-stage calciner, the steam quantity is a decisive factor. The reactor should be operated with as much steam as possible. This implies that for a reactor designed as a bed, it should have the maximum possible surface area. However, even if the heat input argument remains less relevant, a design as a fluidized bed is still recommended.

4 Conclusions

From the simulation results, it is clear that the integration of a solid/solid heat exchanger is necessary because the amount of energy provided in deliverable 1.1 is not sufficient without a solid/solid heat exchanger. With the integration of a solid/solid heat exchanger it is immediately clear that the energy of the outgoing sorbent stream from the calciner is needed to heat the sorbent stream entering the calciner. This is therefore in competition with the second stage calciner, in which the waste heat is used for steam generation.

Simulations have shown that the energy saved by the reduction in conversion in the first calciner, which is achieved by a second-stage calciner, is low compared to the solid/solid heat exchanger. It is shown that only from a conversion of approx. 75 % in the first calciner, a steam mass flow can be heated, so that this does not cool the sorbent flow and enough heat is still available for a reaction in the second-stage calciner. However, the energy savings are low compared to the solid/solid Heat Exchanger. Furthermore, the experimental work has shown that the 900 °C achieved in the first calciner under CO₂ fluidization is not sufficient to achieve any appreciable conversion. At least 910 to 920 °C are required to achieve a meaningful reaction rate. From a design point of view - material properties - it became apparent during the processing in deliverable 5.2 that the calciner temperature must not be higher than 880- 900 °C. From the point of view of reaction and material technology, it follows that calcination must be carried out with steam, irrespective of the process variants.

Tests were carried out for three particle fractions 0.1-0.3/0.2-0.5/0.3-0.7 mm with 100 % steam/N₂ and CO₂ as fluidization medium. Using the results, it can be shown that there is a deviation of 10 % from the equilibrium with steam and 50 % with nitrogen. The amount of CO₂ released from the limestone depends solely on how quickly the steam flushes the CO₂ out of the reactor. This is due to the equilibrium limitation. The maximum achievable partial pressure is determined by the temperature - which is determined by process conditions and design. The amount of steam alone determines how much CO₂ is released. Considering these aspects, it becomes clear that 100 % steam fluidization is reasonable. Any amount of CO₂ fluidization in the first calciner does not lead to any further increase in conversion. From this it can also be deduced why smaller particles have lower CO₂ release rates than larger particles. Due to the higher flow rates, the CO₂ released by the reaction can be flushed out of the reactor more easily.

As part of the deliverable, the extent to which the use of steam in the Indirectly Heated Carbonate Looping process is useful was examined. In this context, not only the case of the second-stage calciner was examined, but also a cross-process look was taken to see which process variance is most sensible from an energy point of view. The experimental investigations showed that the application of the second-stage calciner is possible in principle. Based on the simulated results, direct steam calcination was also carried out. It was shown that the amount of steam plays a decisive role in the reaction rate. As shown from the simulation results, the greatest energy savings can be achieved with a combination of solid/solid heat exchanger and direct steam calcination at 850 °C. Instead of integrating another reactor into the process, calcination should take place in the first reactor under 100 % steam atmosphere fluidization.

Within the scope of the deliverable, it was successfully demonstrated in which way steam can be usefully applied in the carbonate looping process. And direct steam fluidized bed calcination as a design proposal was made.

5 References

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