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# D8.2
# Oxyfuel suspension calciner test results

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| Abstract |
|---|
| This deliverable (D8.2) summarizes the calcination tests conducted within work package 8 (WP8) of CEMCAP project. The main objective was to perform reference air and oxyfuel calcination tests, to evaluate a possible shift of calcination temperature in a $CO_2$-rich oxyfuel environment. The oxyfuel tests were further extended to evaluate the most industrially relevant operational parameters like temperature, residence time and atmosphere. The test results show the average shift of 50-70 K for oxyfuel calcination, which is in line with studies publically available. Provided the higher temperature, reference calcination level ($\geq$90 %) could be achieved within existing suspension calciner conditions. For the test conducted with fuel addition, the reference calcination level ($\geq$90%) for air case was achieved at temperature of 860°C (similar to the temperature reported for industrial calciner), while for oxyfuel case the temperature level up to 940°C was required to achieve similar level of calcination.<br>The evident problem of amplified formation of deposits at higher temperatures in the calciner could not be linked to increase sintering of raw meal itself. From that point of view retrofitting of existing calciners to oxyfuel operation seems possible. However, to clarify the deposit issue, there should be invested some effort to investigate the influence of ashes derived from burning (alternative) calciner fuel at oxyfuel calcination temperature.  Further research and development work should be focused on pilot scale trials in real calciner (hardware) configurations and modeling studies for retrofitting options. |

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# 1    INTRODUCTION

This deliverable (D8.2) summarizes the calcination tests conducted within work package 8 (WP8). In this report the term calcination refers to the chemical decomposition of limestone ($CaCO_3$) to lime ($CaO$) and carbon dioxide ($CO_2$).

The major objective of the work package is to assess the impact of oxyfuel process environment on calcination. A broad variety of test parameters, like temperature, residence time and atmosphere are chosen to represent industrial relevant boundary conditions.

Figure 1 shows the sketch of the industrial cement production process. The major parameters, functions and process reactions occurring in the individual sections are summarized in Table 1.
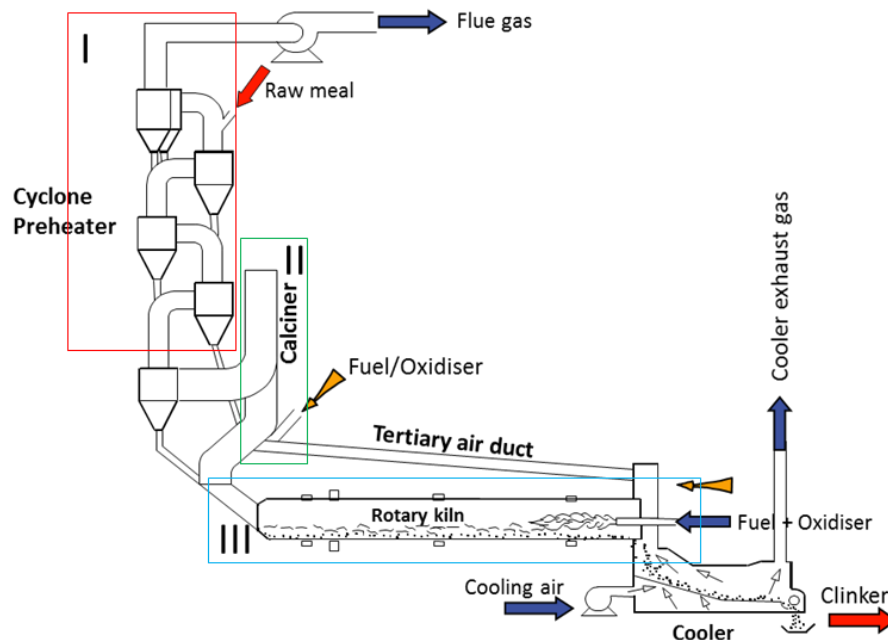


*Figure 1: Best available technology (BAT) cement plant [2]; Preheater cyclones (I), calciner (II) and Rotary Kiln (II)*

After grinding, the raw meal is heated in different cyclone stages and partly calcined up to 20 %. Then, the major calcination reaction occurs inside the calciner. The endothermic reversible equilibrium reaction of calcium carbonate dissociation (calcination reaction) is shown below:

$$CaCO_3 \leftrightarrow CaO + CO_2 \tag{I}$$

The reaction enthalpy $\Delta H \approx 1800$ kJ/kg of $CaCO_3$ and the dissociation temperature strongly depend on the partial pressure of $CO_2$ in the surrounding atmosphere. Since it is a reversible reaction, the dissociation temperature is also referred to as equilibrium temperature. The dissociation temperature becomes higher with increasing partial pressure of $CO_2$. The dissociation reaction proceeds only when the temperature of the raw meal particles exceeds the equilibrium temperature. Increased $CO_2$ concentration (owing to oxyfuel mode) therefore increases the decomposition temperature.

Table 1: Major parameters at different sections of the cement production process (typical range summarized from various literatures [1, 2 and 3])

|  | Preheater cyclones | Calciner | Rotary Kiln |
|---|---|---|---|
| Gas Temperature [°C] | 350-950 | 850-1100 | 1200-2000 |
| Particle Temperature [°C] | 200-750 | 800-900 | 1200-1550 |
| Residence time | 20 s | 3-9 s | Up to 30 minutes |
| Major reactions | Moisture evaporation (100-400 °C) combined water release (400-650 °C) $MgCO_3$ dissociation (650-750 °C) up to 20 % calcination at exit | $CaCO_3$ dissociation (750 °C-900 °C) 90-95 % calcination at exit | Clinker formation |

The calcination tests were carried out in an electrically heated entrained flow reactor at IFK, USTUTT. The tests are conducted in both, air and oxyfuel mode. The first aim of the tests is to establish the reference calcination condition for both air and oxyfuel mode. This condition is defined as to achieve ≥90 % calcination within a residence time of 6 s. The calcination tests are performed at various temperatures to evaluate the correlated temperature shift related to increased $CO_2$ concentration in an oxyfuel operation mode (80 vol% $CO_2$) in comparison to air operation (20 vol% $CO_2$).

The objectives of the tests are further extended to evaluate;

- Influence of temperatures
- Influence of residence times
- Influence of raw meal particle size distributions
- Influence of $CO_2$ concentrations
- Influence of water vapor ($H_2O$)
- Influence of fuel addition

The solid samples were extracted during these tests and analyzed to determine the degree of calcination achieved under different test conditions.

## 2 EXPERIMENTAL METHODOLOGY

In this chapter the experimental methodology is summarized. It has been previously reported as different WP milestones;
MS8.1 Experimental matrix and methodology for oxyfuel calciner tests (M6), USTUTT
MS8.2 Completion of modification of experimental and sampling equipment (M9), USTUTT
MS8.3 Start of compilation and exchange of data to WP6 and WP12 (M12), USTUTT
MS8.4 Completion of oxyfuel calciner tests (M24) - Memo, USTUTT
MS8.5 Submission of de-carbonisation degree analysis results from VDZ to USTUTT (Memo, VDZ).

## 2.1 Test facility

The calcination tests were carried out in an electrically heated entrained flow reactor located at IFK, USTUTT. The facility has been extensively used for combustion and emission characterization of pulverized fuel firing in the past. The facility has to simulate the industrial calciner (see, Figure 1, II). The facility has been modified and adapted to perform the calcination tests. Figure 2 shows the modified facility. In the following the calcination tests are referred to as entrained calcination tests.

The reactor is an electrically heated ceramic tube (0.2 m in diameter and a length of 2.5 m). In this tube, a certain temperature profile can be established by a bulk heating chain. The maximum electrical power input is 58 kW. There are five heating zones (2 x 12 and 3 x 8 SiC - heating elements) whereby a maximum possible temperature of about 1400 °C can be reached. The solid (raw meal) is dosed by a volumetric screw feeder allowing a range of mass flow up to 5 kg/h. The total residence time (from injection point to reactor outlet) can be adjusted by varying the total gas mixture injected into the reactor.

The modification of the facility includes:

- gas mixing station to prepare gas mixtures relevant for air and oxyfuel modes

- adjustments to the feeding system to inject the raw meal into the reactor

- heating system to preheat the raw meal and gas mixture before injection

- thermocouples at raw meal and gas injection lines to measure temperature

- thermocouples at various locations inside the reactor to measure temperature

- a vertically shifted and temperature regulated lance to collect solid samples at any desired location inside the reactor
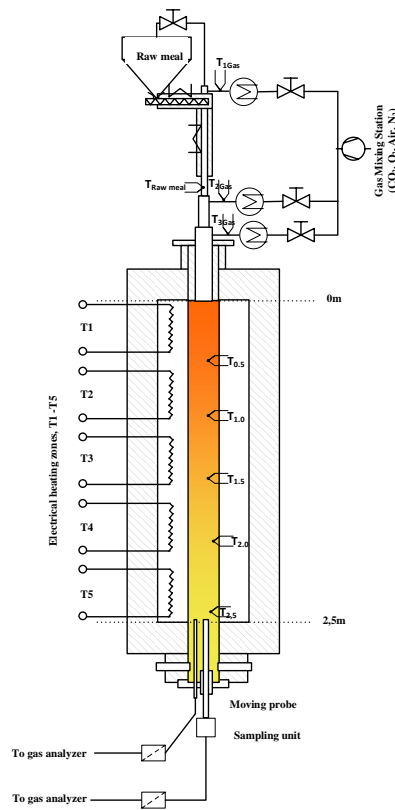
Figure 2: Modified facility suitable for entrained calcination tests

## 2.2 Test parameters

The most important parameters for the entrained calcination tests were atmosphere, temperature and residence time. These parameters were chosen based upon deliverable 8.1 [1, 2] to represent relevant industrial calciner conditions.

Table 2: The range of test parameters

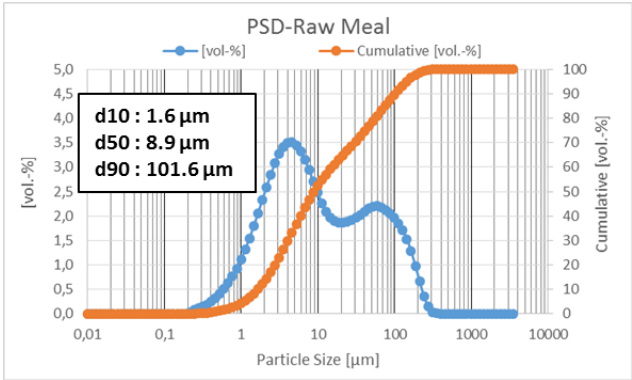| Test | Temperature | Atmosphere | Residence time |
|---|---|---|---|
| Air calcination (AF) | 780 °C to 920 °C | 20 vol% $CO_2$ | 3-9 s |
| Oxyfuel calcination (OF) | 880 °C to 960 °C | 80 vol% $CO_2$ | 3-9 s |

Atmosphere: The gas composition of 20 vol% $CO_2$, 3 vol% $O_2$ and remaining $N_2$, represents the air mode calcination. In oxyfuel mode the gas composition is 80 vol% $CO_2$, 3 vol% $O_2$ and the rest $N_2$.

Temperature: The theoretical decomposition temperature of $CaCO_3$ in the air mode atmosphere is 795 °C. The maximum temperature in existing industrial air calciners is 880 °C - 900 °C. The temperature range for the air mode calcination tests was chosen to cover this temperature range. The theoretical decomposition temperature of $CaCO_3$ in oxyfuel mode is 884 °C. Considering this fact the higher temperatures for the oxyfuel case calcination tests were chosen.

Residence time: The total residence time from raw meal injection point (i.e. 0 m) to sampling point (i.e. 2.5 m) is established by the total gas volume flow. Different residence times are realized by sampling at different positions down the injection point.

Raw meal: Raw meal supplied by Arrigorriaga Factory was used for the entrained calcination tests. The chemical composition of this raw meal is shown in Table 3.

Table 3: Chemical composition and particle size distribution of raw meal

| Raw Meal Composition | [wt.-%] | Particle size distribution |
|---|---|---|
| Moisture (105°C) | <0,1 | |
| $CO_2$ (950°C/IR) | 31.2 | |
| $H_2O$ (950°C/IR) | 1.35 | |
| $Al_2O_3$ | 3.83 | |
| CaO | 42.3 | |
| $Fe_2O_3$ | 2.01 | |
| $K_2O$ | 0.968 | |
| MgO | 0.630 | |
| $MnO_2$ | 0.035 | |
| $Na_2O$ | 0.274 | |
| $P_2O_5$ | 0.065 | |
| $SO_3$ | 0.997 | |
| $SiO_2$ | 13.2 | |
| $K_2O$ | 0.968 | |
| $TiO_2$ | 0.151 | |



## 2.3 Establishment of test cases

The following procedure was applied to establish each test case.

- The gas atmosphere for air and oxyfuel mode was established for the chosen total gas flow. The established gas composition varies within a range of ±0.5 vol%.
- A uniform temperature was established along the reactor centerline by adjusting the set temperature of the electrical heating zones (T1-T5, see Figure 2). The temperature reported hereafter is the average temperature inside the reactor (centerline) measured at 5 different locations, namely 0.5 m, 1.0 m, 1.5 m, 2.0 m and 2.5m down the injection point. The temperature fluctuation was within a range of ±5 °C.

- Once the temperature was established, the raw meal was injected into the reactor. After raw meal injection the temperature at the upper section of the reactor slightly decreases (up to 5 °C), depending on the amount of raw meal injected to the reactor. This was adjusted by increasing the set temperature of the heating zone T1 (see Figure 2).

- Since the raw meal feeding rate does not significantly impact the achieved degree of calcination when compared among the same gas flow and temperature (evaluated from the samples collected 2.5 m down the injection point) a raw meal feeding rate of 1 kg/h was arbitrarily chosen for the tests.

- The solid samples for each test case were collected and in parallel the gas composition was continuously measured at the end of the reactor.

In air case, the increase in the $CO_2$ concentration during the tests gives preliminary information about the extent of calcination and was used as conformation to start the solid sampling. In case of oxyfuel, the increase in the $CO_2$ concentration was hard to register (on the background of 80 vol% $CO_2$) therefore the solid samples were quickly analyzed after the test by a method using hydrochloric acid. It gives the conformation to send the samples to the laboratory for further analysis. The different methods that were implemented to evaluate the degree of calcination are briefly described in Appendix A.2.

The samples were analyzed to determine the remaining $CO_2$ content. From this, the degree of calcination for each test case was evaluated using the formula below [4].

$$\text{Calcination} = 1 - \left( \frac{x_{CO_2}^{sample} * \left( 1 - x_{CO_2}^{raw\ meal} \right)}{\left( 1 - x_{CO_2}^{sample} \right) * x_{CO_2}^{raw\ meal}} \right)$$

Where,

$x_{CO_2}^{raw\ meal}$ is the mass fraction of carbon dioxide in the raw meal $[-]$

$x_{CO_2}^{sample}$ is the mass fraction of carbon dioxide in the calcined sample $[-]$

# 3 EXPERIMENTAL RESULTS

## 3.1 Air calcination vs. oxyfuel calcination

Figure 3 shows the calcination degree achieved at different temperatures during air calcination (AF) and oxyfuel calcination (OF) tests. The major test conditions are given in Table 4. The calcination degree reported here is evaluated from the samples collected at 2.5 m down the injection point.

Table 4: Test conditions (temperature variation)

| Test case | No preheating | With preheating |
|---|---|---|
| Calcination case | AF and OF | AF and OF |
| $T_{raw\ meal}$ | Room temperature | 150 °C |
| $T_{gas\ mixture}$ | Room temperature | 550 °C |
| Calcination [%] before entering the reactor | Negligible (<1%) | Negligible (<1%) |
| Raw meal fed | 1 kg/h | 1 kg/h |
| Total gas mixture | 10.5 $m^3$(STP)/h | 10.5 $m^3$(STP)/h |
| Reactor temperature | 790 °C-960 °C | 790 °C-960 °C |

By changing the atmosphere from air to oxyfuel mode at the same temperature, for example at 880 °C, the calcination degree is reduced by almost 60 %. The reduction is solely related to the increased partial pressure of $CO_2$ as all other test conditions remain similar.

One of the clear results from this comparison is the higher temperature needed for oxyfuel calcination to achieve similar degrees of calcination compared to the air case. For test case 2 (no preheating), 90 % calcination is achieved around 900 °C in air case (see Figure 3, AF w/o preheating) while in oxyfuel case similar degree (85 %) of calcination is achieved at a temperature around 950 °C (see Figure 3, OF w/o preheating).

Similarly for test case 3 (with preheating), 90 % calcination was achieved around 880 °C in air calcination case (see Figure 3, AF w/ preheating) while in oxyfuel calcination case a similar degree (90 %) of calcination was achieved around 950 °C (see Figure 3, OF w/ preheating). The achieved calcination degree with preheating shows improvement at lower temperatures. However, most importantly, it should be noted that the temperature shift for oxyfuel calcination remains similar. The temperature shift for oxyfuel calcination as shown for the entrained tests is located within a range of 50-70 K. A similar temperature shift has been reported in various literatures (see Table 5), which means, owing to the higher concentration of $CO_2$, the oxyfuel calciner requires higher temperatures in comparison to air calcination.
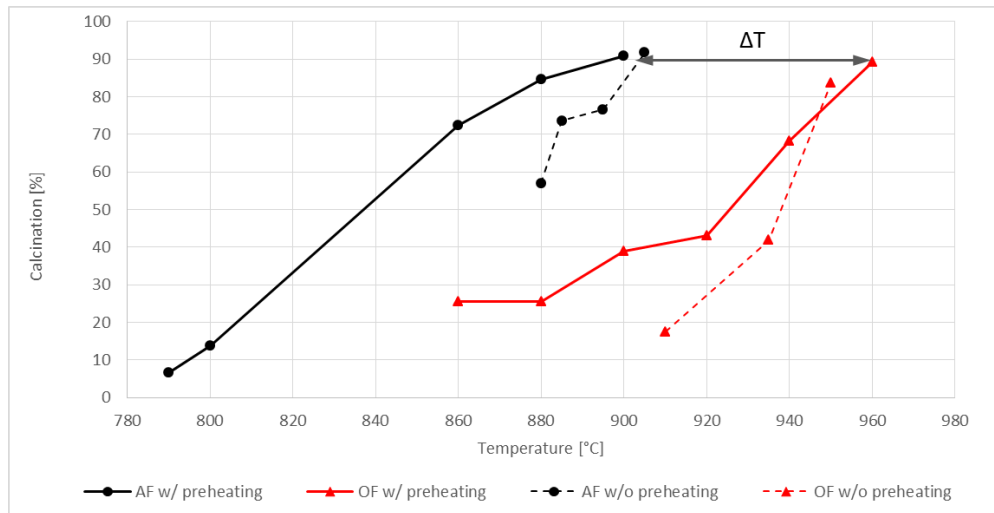
Figure 3: Calcination degree [%] at different temperatures AF (air calcination case) and OF (oxyfuel calcination case)

There are differences in the absolute value of the required ΔT, which apparently arise due to different test setups, the characteristics of the used raw meal, test condition (differences in $CO_2$ concentration referred to as oxyfuel case and residence time available for the calcination process) and other assumptions made for comparative evaluation. Table 5 shows the comparison of ΔT reported in various literatures and established from the performed CEMCAP tests.

Table 5: Comparison of ΔT established form CEMCAP tests and reported in various literature

|  | ΔT [K] | Remarks |
|---|---|---|
| CEMCAP tests, USTUTT *(Figure 3, of this report)* | 50-70 | Entrained calcination test 80-90 % calcination 20 vol% $CO_2$ reference air case 80 vol% $CO_2$ reference oxy case Residence time approximately 6 sec. |
| ECRA results [5] | 80 | Lab tests |
| Pilot scale trial (FLSmidth's R&D Plant) [6] | 60-70 | >92 % calcination The maximum $CO_2$ level reach for oxy case was 66 vol%, dry |

## 3.2 Oxyfuel calcination temperature

The temperature shift for oxyfuel calcination, i.e. higher calcination temperature during oxyfuel mode to achieve similar degree of calcination remains comparable among different test scenarios performed in the frame work of the CEMCAP project. These findings are in line with the theoretical studies, ECRA tests as well as the experiments conducted in different test setups and in the real scale calciner pilot trials. Despite of variations in the test setup and probable difference in the characteristics of the used raw meal during these individual tests, the comparable temperature shift for oxyfuel calcination indicates that this phenomenon is not merely an artifact of a specific test setup. It is clear that to achieve a similar degree of calcination as in air case,

higher temperatures are to be expected under oxyfuel conditions. Now, the question is up to which level does the oxyfuel calcination temperature rise?

The TGA (thermogravimetric analysis) of the raw meal sample was conducted in 20 vol% $CO_2$ atmosphere (reference air case) and in 80 vol% $CO_2$ atmosphere (reference oxy case) with a heating rate of 1 K/min.
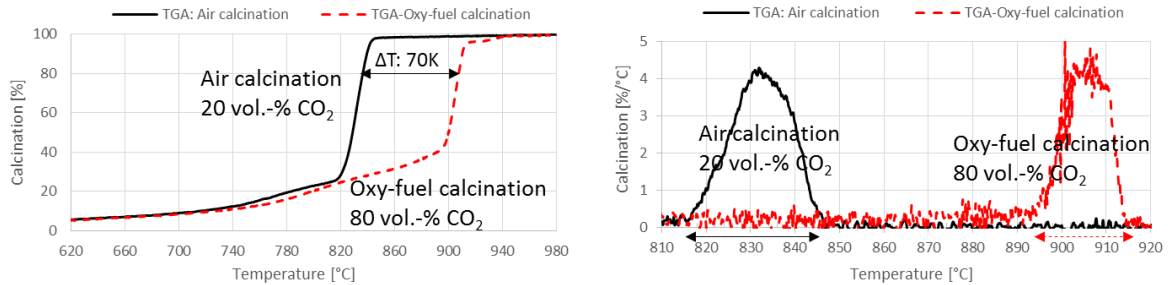


Figure 4: Calcination degree [%] (left) and calcination rate [%/°C] derived from TGA

The degree of calcination which is achieved during air calcination and oxyfuel calcination is similar up to 820 °C. After 820 °C, in the air case, the raw meal quickly releases $CO_2$ and until 840 °C almost complete calcination is observed. While for oxyfuel, the calcination degree slowly rises until 900 °C. After 900 °C the raw meal quickly releases $CO_2$ and until 920 °C almost complete calcination is observed (see figure 4, left). The temperature window of $CO_2$ release under oxyfuel looks even 5-10 °C less than air case, however the release rate is comparable to air case.

It can be well assumed that the temperature reached by the raw meal particles in TGA analysis is reasonably near to the temperature measured as very small amount of sample is used in TGA. To keep the temperature difference between measured temperature and the raw meal particle temperature as low as possible, the low heating rate of 1 K/min was chosen.

The entrained tests for both cases show higher temperature levels to achieve reference calcination levels (i.e. ≥90 %). For air calcination the range of 880-900 °C and in oxy case the range of 940-960 °C.

One of the reasons for the higher temperatures during the entrained tests is apparently the difference in temperature measured and the temperature achieved by the raw meal particles. The heating of the raw meal particles up to their dissociation temperature and the subsequent release of $CO_2$ from the raw meal occurs in entrained condition. The heat transfer to the raw meal particles from the environment depends on the heat transfer characteristics of the test facility itself which in turn is influenced by the physical (e.g. particle size distribution) and chemical characteristics (e.g. composition) of the raw meal, how well they are dispersed inside the reactor and the partial pressure of $CO_2$ in the reaction environment.

In the cement production process, the raw meal is preheated at different cyclone stages. The temperature at the last cyclone stage, i.e. before entering the entrained calciner is around 750 °C. Due to longer retention time and vigorous mixing in cyclones, the raw meal particle temperature is apparently similar to the surrounding temperature. The fuel is burned inside the calciner which provides the necessary energy to proceed the endothermic calcination reaction. The existing (air) calciner has operating temperature levels up to 840 °C-860 °C and is expected to be adequate to achieve a calcination degree ≥90 % at the calciner outlet. The typical upper temperature limit is 880-900 °C at the calciner outlet. The operating temperatures of existing air calciners are substantially higher than the required theoretical equilibrium temperature to proceed the calcination reaction. Therefore, the calciner operating temperatures in oxyfuel mode are as well

expected to be higher than the theoretically required equilibrium temperature when other conditions remain similar to reference air operating conditions. It is clear that even within the maximum operating temperature range of existing (air) calciners the achieved calcination level at the calciner outlet would be substantially lower when the environment is changed to oxyfuel. The increase in residence time alone is not adequate to achieve similar degrees of calcination at the calciner outlet. The increase in temperature is mandatory.

## 3.3 Calcination vs. residence time

Figure 6 shows the calcination degree achieved at various temperatures in oxyfuel case. For each temperature case the total gas flow was varied in order to establish different residence times. The corresponding residence time is approximated from the average gas velocity (calculated) inside the reactor. The approximated residence time varied from 6 to 13 s. The other parameters and the sampling position were similar. The calcination degree is determined from the sample collected at 2.5 m down the injection point.
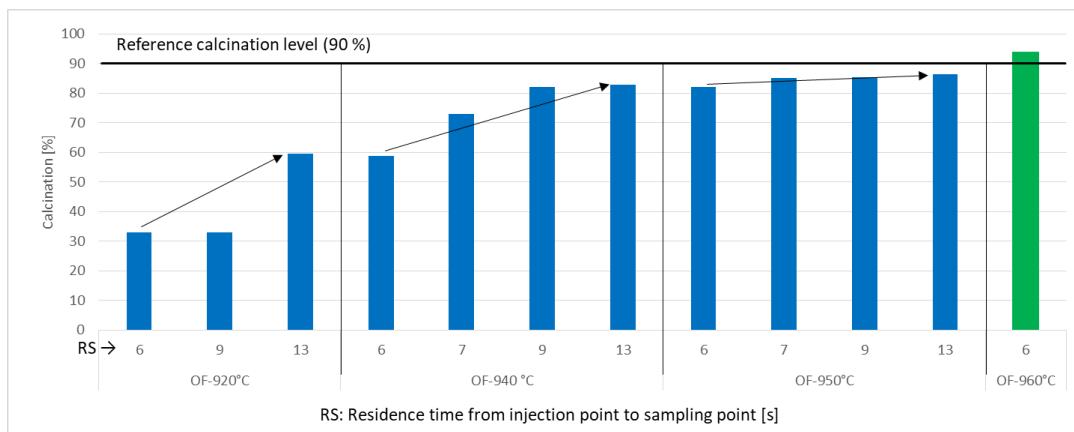


Figure 5: Calcination degree [%] in oxyfuel case at different temperatures and residence times

The residence time is in the range of 3-9 s in most industrial calciners. When comparing the calcination degree achieved within 6 s in different temperature cases, it is clear that to achieve the reference level of calcination (i.e. ≥90 %) in oxyfuel case a temperature ≥960 °C is required. At temperatures lower than 960 °C, for instant at 920 °C, the calcination degree achieved within 6 s is in the range of 30 %. With increased residence time from 6 to 13 s the calcination degree increased up to 60 %. The increase in calcination between 6 and 13 s is around 4,3 %/s at 920 °C, 3,8 %/s at 940 °C and 0,6 %/s at 950 °C.

At temperatures below 960 °C the increase in residence time alone could not achieve the reference calcination degree. To achieve the reference calcination degree within the typical residence time range of existing calciners the higher temperature is required. In contrast to industrial operation, the preheating levels of raw meal and gas mixture were lower in the entrained flow calcination tests. That means, that after entering the reactor, at first the temperatures had to be increased until the raw meal particles reached the equilibrium temperature. That heat transfer process needs time depending on the temperature gradient between the surrounding and the particles. Higher temperature means quicker heating up of the raw meal. So the higher temperature of the reactor is not to start the calcination reaction itself but to increase the heat transfer and thereby the reaction rate.

The temperature of 960 °C represents the oxyfuel calcination case with ≥90 % calcination. In air calcination case the temperature of 900 °C is required to achieve the same degree of calcination.

Calcination ≥90 % is chosen as reference, because it represents the calcination degree at the exit of existing industrial calciners.

Table 6: Test conditions (residence time variation)

| Calcination case | AF | OF |
|---|---|---|
| $T_{raw\ meal}$ | 400 °C | 400 °C |
| $T_{gas\ mixture}$ | 550 °C | 550 °C |
| Calcination [%] before entering the reactor | Negligible (<1%) | Negligible (<1%) |
| Raw meal fed | 1 kg/h | 1 kg/h |
| Total gas mixture | 10 m³(STP)/h | 10 m³(STP)/h |
| Reactor temperature | 900 °C | 960 °C |

The variation of the residence time by changing the volumetric flow is limited due to restrictions of the test rig. So for two reference cases, air calcination (10AF-900 °C) and oxyfuel calcination (10OF-960 °C), the raw meal samples were collected at different locations, namely 1 m, 1.5 m, 2.0 m and 2.5 m down the injection point. Each sampling location represents a certain residence time in the reactor. The corresponding residence time is approximated from the average gas velocity (calculated) inside the reactor. The major test conditions are shown in Table 6.



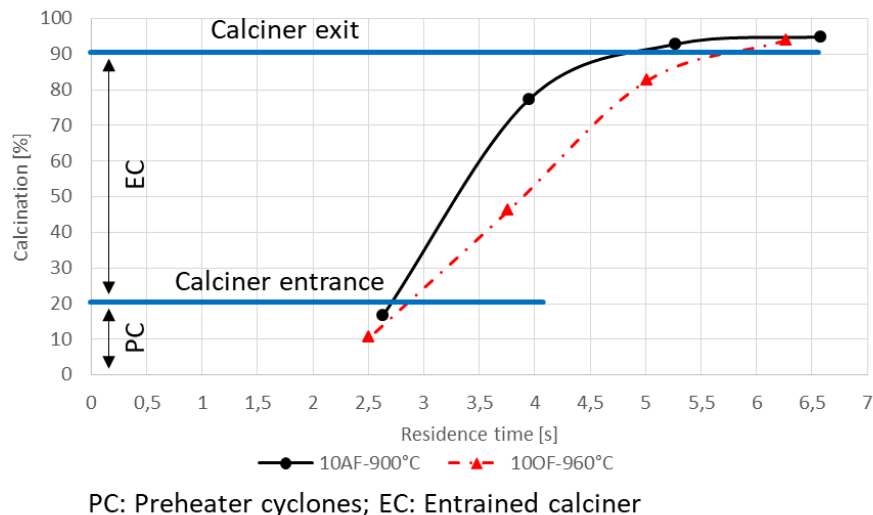PC: Preheater cyclones; EC: Entrained calciner

Figure 6: Calcination degree [%] at different residence time down the injection point

Figure 6 shows the calcination degree achieved at different residence times. For both cases, 20 % calcination is achieved within 3 s. The calcination increases linearly in the beginning and flattens out after approximately 5 s.

In industrial cement calciners, the raw meal is preheated in cyclones (at different stages) and almost 20 % calcination is achieved during this preheating process. Assuming the logarithmic progress (see Appendix B, Figure 21) the reference initial point is determined, i.e. the location where ≈20 % calcination is achieved. This location is therefore considered as the calciner entrance. With this assumption, the calcination degree and calcination rate [%/s] vs. residence time for the given test conditions is derived.
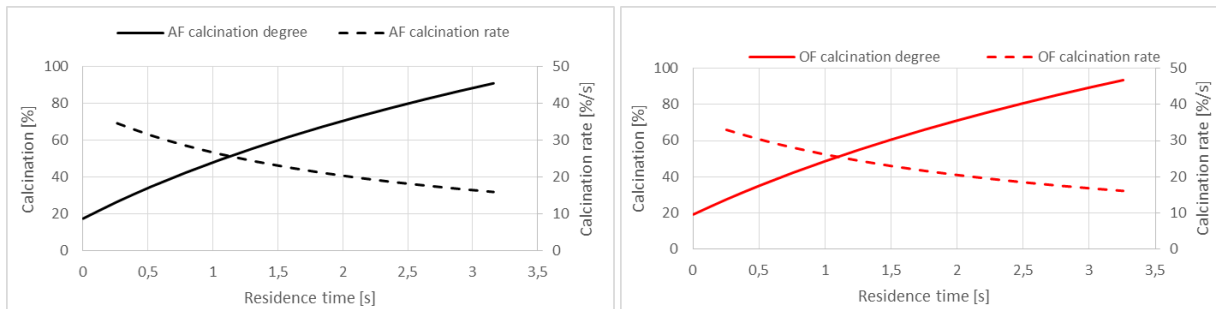
Figure 7: Calcination degree [%] and calcination rate [%/s] vs. residence time, air case (left) and oxyfuel case (right)

In air case 95 % calcination is achieved within a residence time of 3.2 s and the calcination rate decreases from 38 %/s at the beginning to 12 %/s at the end (see Figure 7, left). To achieve a similar degree of calcination in oxyfuel case a residence time of 3.3 s is required and the calcination rate ranges from 36 %/s to 11 %/s. (see Figure 7, right).

Provided the higher temperature and with the other parameters being similar among air and oxyfuel case, it is clear that a similar calcination rate is achieved. The only way to overcome the hindrance on calcination reaction due to increased $CO_2$ partial pressure is the temperature increase. The raw meal particles start to calcine (i.e. release $CO_2$) as soon as they reach the temperature threshold to overcome the equilibrium $CO_2$ partial pressure.

## 3.4     Influence of $CO_2$ concentration

The concentration of $CO_2$ is the major parameter for the related temperature shift in oxy case. Figure 8 shows the calcination degree achieved at various $CO_2$ concentrations. The major test conditions are listed in Table 7.

Table 7: Test conditions (CO2 variation)

| Calcination case | 10-940°C and 10-920°C |
|---|---|
| Traw meal | 400 °C |
| Tgas mixture | 550 °C |
| Calcination [%] before entering the reactor | Negligible (<1%) |
| Raw meal fed | 1 kg/h |
| Total gas mixture | 10 m3(STP)/h |
| Reactor temperature | 940 °C and 920 °C |

The calcination degree decreases with increase in $CO_2$ concentration at both temperatures, but follows a slightly different trend (see figure 8). The calcination degree is almost similar at 920 °C and 940 °C with 20 % $CO_2$ in the surrounding atmosphere. At the other $CO_2$ concentrations (namely, 40, 60 and 80 %) the calcination degree is comparatively higher at 940 °C. The difference is about 10 %, 30 % and 35 %, respectively with 40 %, 60 % and 80 % $CO_2$. The trend apparently indicates that the temperature of 940 °C is adequate enough to reach the required calcination degree for a $CO_2$ concentration level up to 60 vol% dry, while 920 °C might be inadequate to achieve reference calcination levels when $CO_2$ concentration is increased above 20 vol% dry $CO_2$. This clearly demonstrates the impact of $CO_2$ concentration on the

calcination degree and associate higher temperature requirements to achieve similar degree of calcination when the $CO_2$ concentration in the surrounding atmosphere is increased.
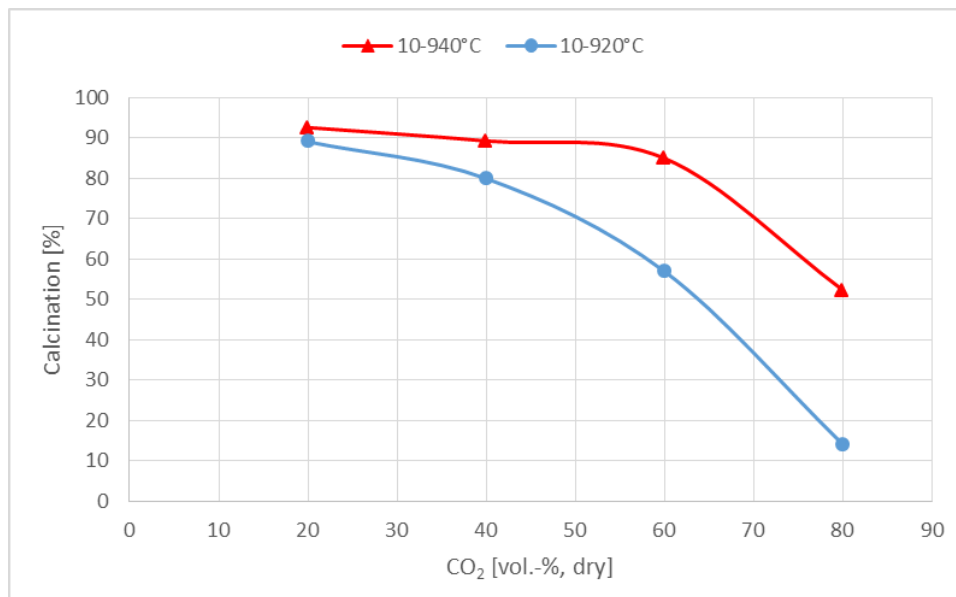


Figure 8: Calcination degree [%] at various $CO_2$ concentration

## 3.5 Influence of particle size distribution

The particle size distribution of the raw meal particles does have an impact on the calcination. The test results discussed above are performed with the raw meal sample as received from the supplier. The particle size distribution is within the range of raw meal used in the industrial cement production process.

To evaluate the influence of particle size distribution a finer fraction of raw meal was prepared by sieving with a 50 µm sieve. The particle size distribution of the raw meal sample collected after the sieving is shown in Table 8.

Table 8: Test conditions (particle size variation)

| Calcination case | Oxyfuel (OF) | Oxyfuel (OF) |
|---|---|---|
| $T_{raw\ meal}$ | 400 °C | 400 °C |
| $T_{gas\ mixture}$ | 550 °C | 550 °C |
| Calcination [%] before entering the reactor | Negligible (<1%) | Negligible (<1%) |
| Raw meal fed | 1 kg/h | 1 kg/h |
| Particle size distribution | $d_{10}$: 1.6 µm<br>$d_{50}$: 8.9 µm<br>$d_{90}$: 101.6 µm | $d_{10}$: 1.5 µm<br>$d_{50}$: 6.4 µm<br>$d_{90}$: 30.4 µm |
| Total gas mixture | 10 m³(STP)/h | 10 m³(STP)/h |
| Reactor temperature | 940 °C | 940 °C |

The $CO_2$ content in the resulting raw meal sample was 35.3 wt.-%. The reference calcination scenario (i.e. with calcination ≥90%) for oxyfuel case was established at 960 °C. The test with

For oxyfuel calcination case $CO_2$ concentration is expected to be 80 vol% dry. Presence of water vapor reduces the actual partial pressure of $CO_2$ which potentially influences the calcination rate. Figure 10 shows the calcination degree at various residence times at 940 °C. In oxyfuel case with water vapor, the residence time is shorter owing to increased total gas volume flow due to addition of water.

It shows the comparison among the cases with water vapor (10OF-940°C-10%$H_2O$) and without water (10OF-940°C). For both cases the $CO_2$ vol% dry remains similar (80 %) whereas the addition of water vapor decreased the actual $CO_2$ content to about 73 vol% (wet). The calcination degree at the end of the reactor increases by almost 10 % in presence of water whereas the calcination rate increase from 20-7 [%/s] i.e. without water to 27-10 [%/s] with water (see Appendix B, Table 21). Compared to the results reported in section 3.4 the achieved calcination degree with water vapor is higher at the same actual partial pressure of $CO_2$. However, taking into account that the test with variation of the $CO_2$ content was conducted with raw meal as received in contrast to the finer fraction which was used in this test, the results are comparable. The increase in the calcination rate is basically related to the decrease of actual $pCO_2$ due to dilution from water vapor.
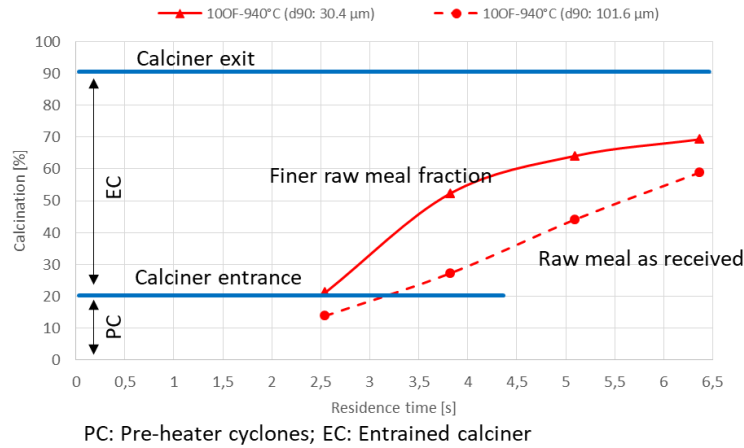


PC: Pre-heater cyclones; EC: Entrained calciner
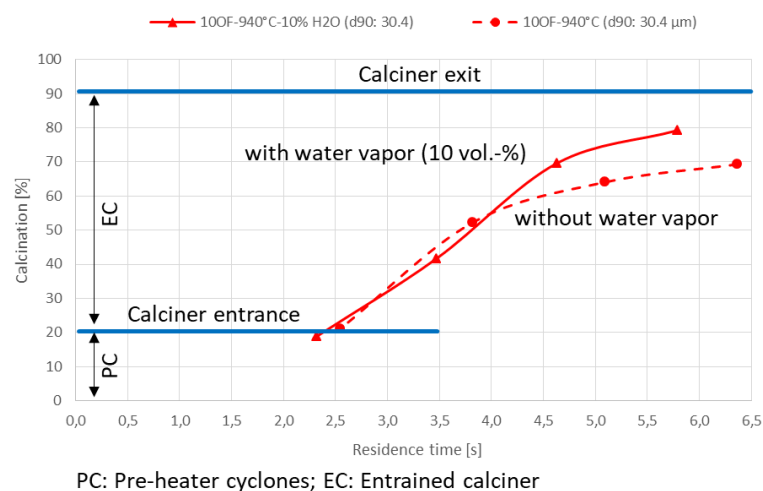
Figure 10*: Calcination degree [%] at different residence time down the injection point during oxyfuel case at 940 °C*

In real calciners the water vapor content could be in a range of 10-12 vol% depending upon the fuel and recirculation. Instead of concentration of $CO_2$ as vol% dry, the actual partial pressure of $CO_2$ influences the calcination rate.

## 3.7 Influence of high temperature on particles

One of the concerns about increasing the temperature for oxyfuel calcination is the risk of sintering or deposit formation which would eventually lead to blockage/plugging of the preheater cyclones. Sintering and/or deposit formation is enhanced when molten species are formed. Such a phenomenon was not experienced/observed during the tests. The raw meal particles were sampled by a suction probe when entrained inside the reactor. The particles were later embedded in resin and prepared for the electron microscopic analysis. The raw meal and calcined raw meal particles

were analyzed by using the scanning electron microscope (see Figure 11). There was no noticeable difference observed that could be linked to enhanced sintering.

The reactions that follow after the calcination process involve formation of molten intermediates as the temperature rises. The higher temperature requirement in oxyfuel case is to complete the calcination reaction itself, therefore probably does not initiate formation of molten intermediates.



Figure 11: Raw meal and calcined raw meal particles under scanning electron microscope

With raw meal alone there was no strong evidence that could be linked to increase sintering. Nevertheless, the behaviour of fuel ash from calciner fuel should be considered. At high temperatures, the fuel ash could be the reason for enhanced deposit formation. T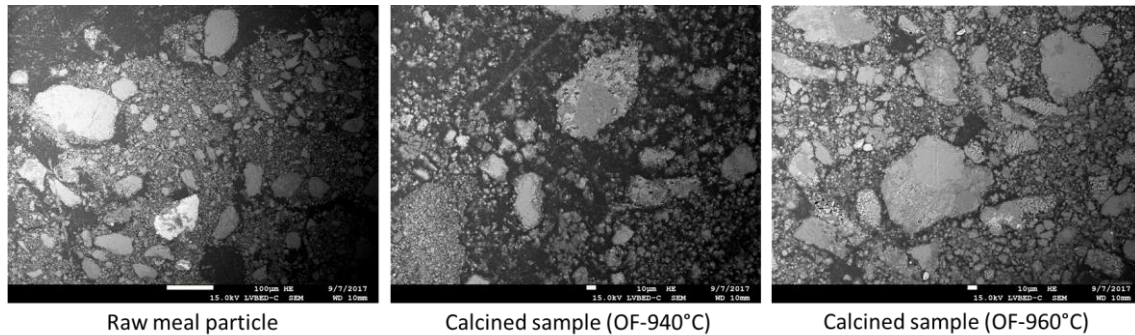he elements K, Na, Cl and S, are prone to form sticky deposits and are the major cause for plugging of cyclones. The existence of sulfur and alkali cycles in the preheater-calciner-kiln system is worsening this problem because thereby the concentration of sulfur and alkalis is increased significantly. Additionally this problem could be even more severe in oxyfuel mode due to lower flue gas volume flows and therefore even higher concentrations of sulfur and alkalis in the mentioned cycles.

## 3.8    Tests with fuel addition

Table 10 summarizes the temperature shift as well as actual temperature reported for oxyfuel calcination tests reported in the earlier section of this report. Temperature shift for oxyfuel is comparable among different tests (see Table 10). The actual temperature however varies according to heat transfer characteristics of the given test facility. This apparently explains the difference in temperature reported as required oxyfuel calcination temperature found in various literature [1, 3, 4, 5].

An electrically heated reactor was implemented for the tests. The power of the reactor is rated as 20 kJ/s. The energy supply of the reactor is substantially higher than the endothermic energy requirement for the calcination reaction (for raw meal mass flow and total gas mixture implemented during the test). The thermo- and fluid dynamic processes inside the reactor are complex. The gradients of temperature and velocity of the gas mixture and raw meal particles are highest directly after injection. That means there is a zone of intense turbulence where the flow velocity is decreasing while the temperature is increasing. In that zone the convective heat transport is supported by turbulence and therefore relative velocity between particles and gas. The same applies for the conductive heat transport due to a lot of contact between the particles. After the injected particle jet has re-attached to the reactor wall a laminar flow is assumed and radiation is the main source of heat transport. The consequence of that is that it is difficult to tell when and where inside the reactor the raw meal particles reach the equilibrium temperature and the

calcination reaction begins. After that point the energy to maintain the reaction has to be provided by the test facility. The temperature of the surrounding has to be sufficiently higher than that of the particles to transport enough energy.

Table 10: Comparison of CEMCAP test results with previous studies

| Source | Temperature shift in comparison to air calcination | Oxyfuel calcination temperature | Remarks |
|---|---|---|---|
| CEMCAP tests, USTUTT (Figure 3, of this report) | 50-70 K | 960 °C >90 % calcination 80 vol%, dry $CO_2$ | Entrained calcination |
| CEMCAP test, USTUTT (Figure 4, of this report) | 70 K | 910 °C >90 % calcination 80 vol%, dry $CO_2$ | Thermogravimetric tests heating rate of 1 K/min (TGA) |
| Pilot scale trial (FLSmidth's R&D Plant) [6] | 60-70 K | 926 °C 95 % calcination 942 °C 98 % calcination 54-58 vol%, dry $CO_2$ | Entrained calcination Pilot scale trial |
| ECRA Studies | 80 K | 950 °C >80 % calcination $pCO_2$ 0.8 bar | Lab studies |

The tests performed at IFK, USTUTT (reported in earlier section of this report) shows comparable temperature shifts as reported from oxy-fuel calcination pilot scale trials at FLSmidth's R&D Plant. However, the actual temperature required for oxyfuel calcination, evaluated from the USTUTT tests, are higher (960°C) in comparison to pilot scale trial (926°C-942°C) (FLSmidth's R&D Plant) [6] . However, while comparing the USTUTT test results with the pilot scale trial (FLSmidth's R&D Plant) it should be noted that the $CO_2$ concentration representing oxyfuel for the pilot scale trial by FLSmidth's is lower (54-58 vol.-% $CO_2$) in comparison to USTUTT tests (80 vol.-% $CO_2$).

One of the reasons for the higher temperature in the tests of USTUTT apparently comes from the limitation of heat transport from the reactor wall towards the entrained raw meal particles. In industrial calciners, the energy required for calcination is provided by the combustion of fuel inside the calciner itself. Energy is then provided within throughout the space of the calcination reaction and not only at the walls of the calciner. Consequently, heat transport is normally no limiting factor with fuel burning inside the calciner. To simulate this scenario, tests with fuel addition were performed. This section of the report summarizes the results from the calcination tests with fuel addition.

Two kinds of fuels have been used for the test completion: a finely milled lignite as a fossil solid fuel and an alternative fuel, finely milled torrified wood (see appendix C for the main properties).

### 3.8.1 Establishment of test cases with fuel addition

The following procedure was applied to establish each test case.

- The gas atmosphere for air and oxyfuel mode was established for the chosen total gas flow. The established gas composition varies within a range of ±0.5 vol.-%.
- At first, a uniform temperature was established along the reactor centerline by adjusting the set temperature of the electrical heating zones (T1-T5, see Figure 2). The temperature reported hereafter is the average temperature inside the reactor (centerline) measured at 5 different locations, namely 0.5 m, 1.0 m, 1.5 m, 2.0 m and 2.5m down the injection point. The temperature fluctuation was within a range of ±5 °C.
- Once the temperature was established, the fuel was injected into the reactor. The fuel and raw meal are fed separately and mixed before injecting into the reactor.
- After fuel injection the temperature at the upper section of the reactor (measured at 0.5 m) increases up to 15 °C, depending on the amount of fuel injected into the reactor. The temperature at the lower sections (>1 m) are not much influenced by the fuel injection.
- The next step was the injection of raw meal.
- If necessary, the temperature of the electrical heating zones (T1-T5, see Figure 2) is again adjusted to maintain the chosen test temperature at the center of the reactor.

The solid samples for each test case were collected and in parallel the gas composition was continuously measured at the end of the reactor. The same procedure was followed for the evaluation of the test results as previously described in section 2.3 of this report.

### 3.8.2 Influence of fuel addition

Introduction of fuel is expected to improve the degree of calcination due to the fact that the fuel combustion is a new source to provide energy inside the reactor to the entrained particles. Whereas, for cases without fuel, radiation from the heated wall is the only source to provide energy with the restriction of heat transport into the reactor. The test results show clear influence of fuel addition on the degree of calcination. Figure 12 a comparison (with (w/) and without (w/o) fuel) for oxy case at 940 °C (OF-940°C) and air case at 880 °C (AF-880°C). Table 11 shows the major test conditions with fuel addition.

Table 11: Test condition (with fuel addition)

| Calcination case | Oxyfuel (OF)-w/ fuel | Air (AF)-w/ fuel |
|---|---|---|
| Reactor temperature | 940°C and 920°C | 880°C and 860°C |
| $T_{gas\ mixture}$ | 550 °C | 550 °C |
| Raw meal | 1 kg/h | 1 kg/h |
| Fuel (German Lignite) | 0.1 kg/h | 0.1 kg/h |
| Total gas mixture | 10 m$^3$(STP)/h | 10 m$^3$(STP)/h |

Near the injection zone calcination is significantly increases with (w/) fuel, resulting in almost 60 % calcination within 2.5 s (see Figure 12, 10OF-940°C-w/ fuel and 10AF-880°C-w/ fuel). For the test without (w/o) fuel the calcination degree at similar residence time is below 20 % (see Figure 12, 10OF-940°C-w/o fuel and 10AF-880°C-w/o fuel).

Additionally, for the tests with fuel addition, the temperature required to achieve the reference calcination level (≥90 % within 6 s) is 940°C, while for the test case with-out fuel addition its was

960 °C (see Figure 5). The lower oxy-fuel temperature is related to the improved heat transfer conditions in presence of burning fuel.

A full de-carbonation and a calcination degree of 100% was not obtained during the tests. Indeed it is not common to reach 100% calcination in industrial calciners operated in normal air mode. Often a calcination degree of about 90% is achieved at the exit of the calciner. 100% calcination is then reached in the rotary kiln. The temperature required for 100% calcination is however an important parameter for process modelling. By extrapolation of the experimental results, the temperature required for 100% calcination was estimated to about 960°C in oxyfuel mode with fuel injection. The extrapolation assumes linear increase.
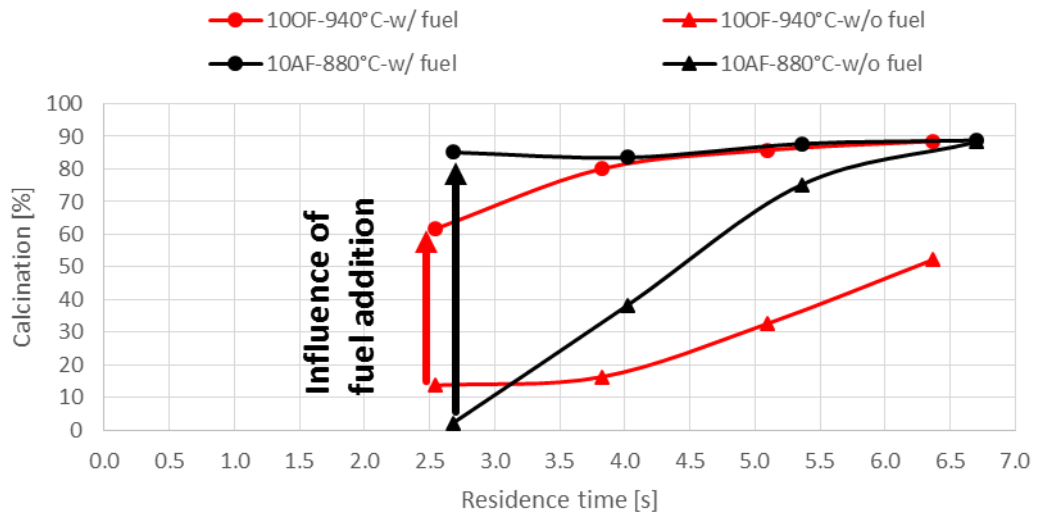


Figure 12: Calcination degree [%] at different residence time down from the injection point, for test with (w/) fuel and without (w/o) fuel; OF-940°C (oxy case) and AF-880°C (air case)

Figure 13 shows the calcination degree at different temperatures for both air (AF) and oxyfuel (OF) case for tests with fuel addition. With fuel addition, the temperature to achieve reference calcination level during air case is 880 °C and for oxyfuel case, 940 °C. The temperature to achieve reference calcination level was 900 °C and 960 °C, respectively air and oxyfuel case, without fuel addition.
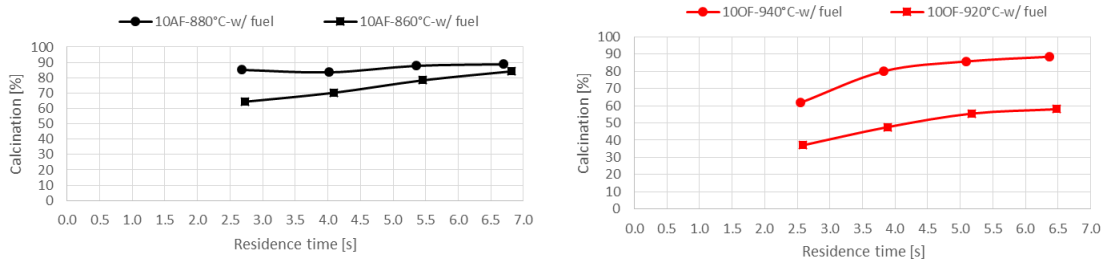


Figure 13: Calcination degree [%] at different residence time down the injection point for test with fuel at different temperatures; left, air case (AF) and right oxy case (OF)

Additionally, similar tests were performed with non-fossil fuel (torrified wood, TW), the amount of fuel was so chosen to have the same energy input as with fossil fuel (German lignite, GL). Figure 14 shows the comparison between the two different fuels during oxy case at same

temperature (OF-940°C). Similar effects were observed on degree of calcination (see Figure 14) when the amount of fuel is chosen so to provide similar amount of energy.

Slightly, faster calcination with torrified wood (see Figure 14), is probably related to higher volatile content in biomass fuel and consequent faster heat release.
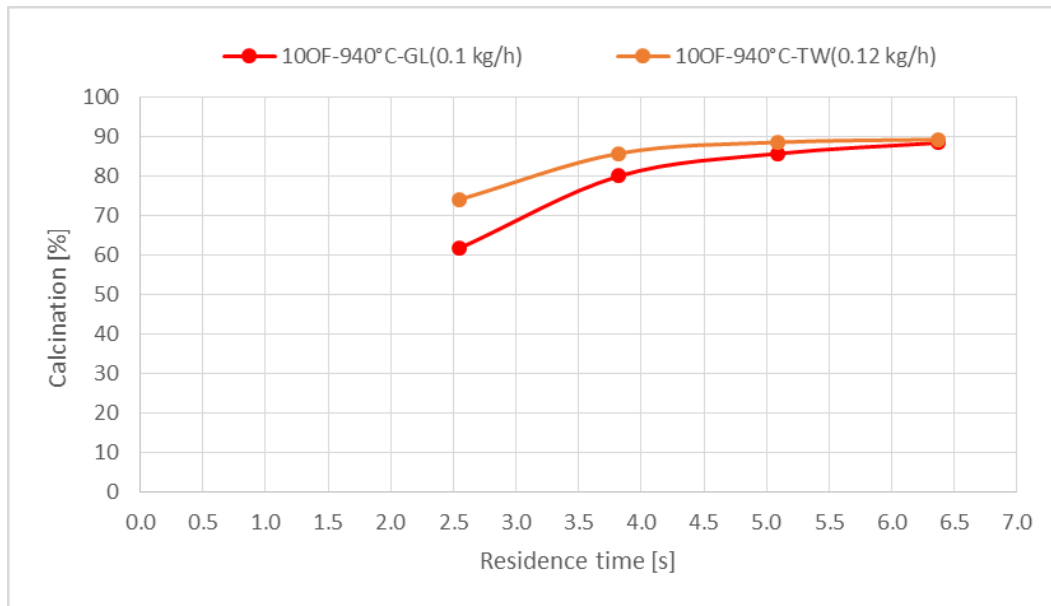


Figure 14: Calcination degree [%] at different residence time down the injection point during oxy case (OF-940°C); comparison with different fuels, German lignite (GL) as fossil fuel and Torrified Wood (TW) as non-fossil fuel

### 3.8.3 Influence of fuel/raw meal ratio

Fuel addition improves the degree of calcination, which is basically due to improved energy transfer from the direct surrounding atmospheres the entrained raw meal particles. The energy transfer from the surrounding atmosphere to the entrained particles initiates the calcination reaction. It depends on flow conditions, available energy in the surrounding and the temperature gradient between the entrained particles and the surrounding atmosphere. The same injection system was used for both test cases (i.e. without and with fuel) so the dispersion of particles (flow conditions/entrainment) are expected to be comparable. In both test cases, without and with fuel, the energy supply is sufficient to support the endothermic calcination reaction. However, for the test cases with fuel addition, the fuel combustion in the vicinity of entrained raw meal particles improves the energy transfer.

The amount of energy released from the fuel combustion is varied with the fuel amount (i.e. fuel to raw meal ratio) in order to evaluate its influence on degree of calcination. Table 12 shows the test conditions with different fuel to raw meal ratios.

Table 12: Test conditions (variation in fuel to raw meal ratio)

| Raw meal [kg/h] | Fuel to raw meal ratio | Remarks | Test temperature | Atmosphere |
|---|---|---|---|---|
| 1 | 0 | No fuel | 920°C and 940°C | Oxyfuel |
| | 0.05 | typical fuel to raw meal ratio in industrial calciners | | |
| | 0.1 | the energy provided from fuel is equivalent to the sum of endothermic energy required for calcination and the energy required to heat the gas mixture at room temperature to calcination temperature | | |
| 1 | 0.3 | fuel to raw meal ratio almost 6 times higher than typical ratio in industrial calciner | 900°C | Oxyfuel |

Fuel addition results in increased degree of calcination at both 920 °C and 940 °C. Within the range of tested fuel to raw meal ratios a temperature of 940 °C was required to reach the reference calcination level of 90 %.

An oxyfuel calcination test at 900 °C, with higher raw meal to fuel ratio up to 0.3 was performed. Temperature of 900°C was chosen for the test because it is the maximum temperature allowed in existing air calciner.
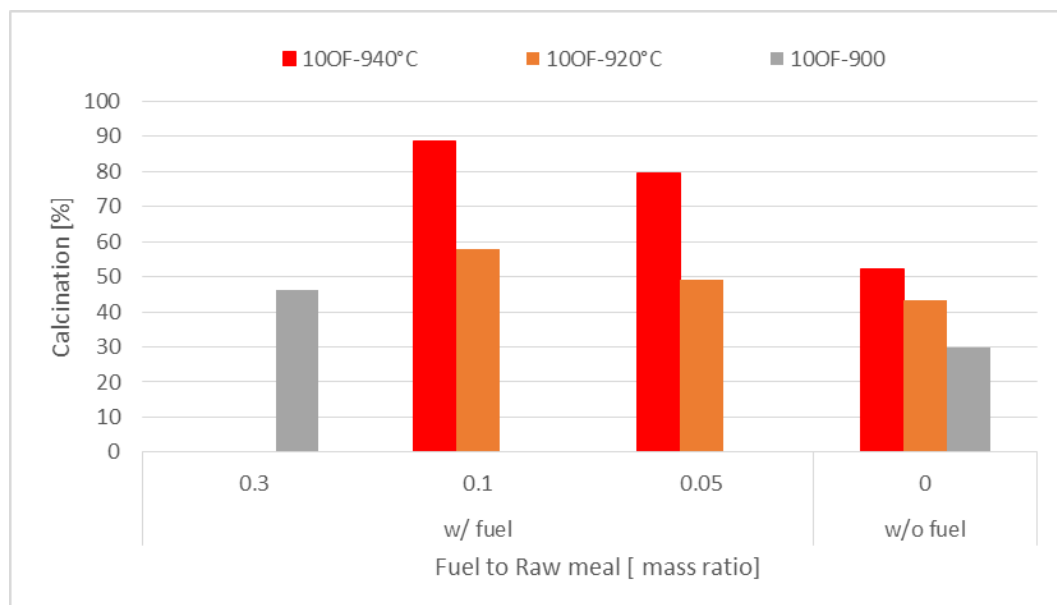


Figure 15: Calcination degree [%]for oxyfuel case at 2.5 m down the injection point at 940°C, 920 °C and 900 °C at different fuel to raw meal ratio

The degree of calcination reaches up to 46% for fuel to raw meal ratio of 0.3 (see Figure 15). Without fuel, the degree of calcination at OF-900°C was around 30% (Figure 15). There was substantial increase in degree of calcination with fuel addition however even by increasing the fuel to raw meal ratio higher up to 0.3 (Figure 15), the reference calcination level of ≥90% could not be achieved at 900°C.

# 4 DISCUSSION: TEST FACILITY AND TEST CONDITIONS

An electrically heated reactor is used for the tests. The temperature inside the reactor is maintained by heating the reactor wall. It was measured by thermocouples and there are certain bias in thermocouple measurements. The thermocouples are influenced by the radiating reactor wall. From the difference in temperature between the reactor wall and temperature measured at the centerline, the radiation bias can be roughly estimated. At the near injection zone (i.e. up to 0.5 m down the injection point) due to radiation bias the measured temperature accounts up to 30 °C higher than actual temperature. While at section below 0.5 m, the temperature difference between reactor wall and temperature measured at the centerline slowly decreases and is almost similar to wall temperature below 1 m.

At this point it has to be considered that $CO_2$, in contrast to nitrogen, is absorbing and emitting radiation and that this causes a different influence on the thermocouples by radiation between air and oxyfuel calcination. Additionally the temperature measured by the thermocouples is dependent on the convective energy exchange between thermocouples and surrounding gas. This exchange is dependent on the velocity of the flow and temperature gradient. So it is not possible to measure the real temperature of the entrained raw meal particles. The temperature represents the temperature of the surrounding atmosphere and wall radiation.

The tests with fuel addition are conducted with three different fuel to raw meal ratios. The ratio 0.05 is the typical ratio for industrial calciners. The transferability of the calcination temperature established with these test conditions to real oxyfuel calciner operation depends on how well the heat transfer behaviour of a real calciner is reflected in these tests. The direct assessment of heat transfer behaviour of the test facility/conditions was difficult. Following assumptions were considered for the evaluation;

- By establishing reference air calcination test conditions within similar temperature, atmosphere, residence time regime of an industrial calciner, and similar heat transfer characteristics for the test facility are assumed.

- Same test conditions were followed to establish the oxyfuel calcination temperature where the atmosphere was changed to higher $CO_2$ concentration (80 vol.-% $CO_2$).

- This means for the air case and the oxyfuel case the application of the same test conditions here refer to the amount of raw meal, amount of total gas mixture, injection system and preheating level before injecting to the reactor.

With fuel burning the enhanced energy transfer from the surrounding atmosphere to the entrained particles also enhances the calcination reaction. The energy transfer from the surrounding to the entrained particles depends on dispersion of particles (flow/entrained conditions) and temperature gradient between the particles and the surrounding atmosphere. To report an exact temperature from these test is impossible, owing to the fluctuations in temperature measured near the injection zone (in presence of fuel) and possible radiation error of the thermocouple measurements. Considering this fact, for the oxyfuel case, temperature to achieve reference calcination degree of 90% is estimated to be in a range of 920 °C to 940 °C and similarly for air case it is estimated to be in range of 860 °C to 880 °C.

Either with fuel or without fuel, the temperature shift from air case to oxyfuel case is similar. The decrease in actual temperature apparently relates to improved energy transfer to entrained raw meal particles in presence of fuel, which is burnt in the reactor.

# 5 DISCUSSION: TEMPERATURE FOR OXYFUEL CALCINATION

It is well established that the higher partial pressure of $CO_2$ in the surrounding atmosphere increases the decomposition temperature. The shift of 80 K, with 800 °C in air case (20 vol.-% $CO_2$ atmosphere) and 880 °C in oxyfuel case (with 80 vol.-% atmosphere) is a result of increased partial pressure of $CO_2$ in the surrounding atmosphere. In an ideal heat transfer scenario, the calcination temperature should be similar to the theoretical decomposition temperature of $CaCO_3$. From practical point of view, the heat transfer conditions inside industrial cement calciners might not be ideal to achieve sufficient calcination in the theoretical decomposition temperature regime. The temperature reported from industrial calciner practice is the temperature measured at certain locations inside the calciner facility. Typically the temperature is monitored at the outlet of the calciner. Temperatures in the range of 840 °C to 860 °C are reported, adequate to reach the required level of calcination of about 90%. The temperature range of 880 °C to 900 °C is the maximum temperature for calciners in current industrial practice. This is in the range of the theoretical decomposition temperature for $CaCO_3$ in an oxyfuel atmosphere. To facilitate the energy transfer from surrounding to entrained raw meal particles, the oxyfuel calciner temperature needs to exceed this maximum temperature limit, to achieve a similar degree of calcination (90% as in air case) at calciner outlet.

The actual temperature required, when an existing air calciner is retrofitted to an oxyfuel calciner, apparently depends on the heat transfer behaviour of the given calciner. Most of the existing air calciners operate in the range fairly above the theoretical decomposition temperature of $CaCO_3$ for the air case, i.e. about 800°C. A similar situation is to be expected for operating oxyfuel calciners. The temperature for oxyfuel calciners established from the calcination tests discussed in this report are in the range of 920 °C to 940 °C.

Calcination is a fast reaction. Once a raw meal particle reaches the required equilibrium temperature, the calcination is completed within seconds. The peak temperatures in the combustion zone (fuel injection area) might give a window to keep the operating temperature within acceptable limits. Further research should therefore focus on test trials in real calciner (hardware) configurations to further validate actual heat transfer behaviour in oxyfuel atmosphere at industrial scale as well as the modeling studies for retrofitting options.

# 6    CONCLUSIONS AND OUTLOOK

The facility used for pulverized fuel combustion at IFK, USTUTT has been successfully modified to perform entrained calcination tests with heating rates, residence times and temperature conditions relevant for industrial calciners. The modified facility is capable to accommodate both air and oxyfuel calcination scenarios. Prior the tests for comparative evaluation of air and oxyfuel calcination, various parametric tests were performed to validate the suitability of the modified facility to perform entrained calcination tests. The test boundaries are comparable to existing industrial calciner operation practice in terms of residence time, atmosphere (air and oxyfuel) and temperature conditions.

The main conclusions drawn from the calcination tests performed within the framework of CEMCAP are as follows:

- Oxyfuel calcination temperature is up to 70 K higher in comparison to air calcination.

- The temperature shift is comparable among different test setups and conditions.

- Provided the higher temperature, reference calcination level ($\geq$90 %) could be achieved within existing calciner conditions

- Instead of $CO_2$ concentration (as vol%, dry) the actual partial pressure of $CO_2$ in the reaction environment determines the calcination rate- i.e. dilution of $CO_2$ by other gas species (e.g. $H_2O$) lead to higher calcination rates.

- The reference air calcination temperature range established from the tests is 860 °C to 880 °C and corresponding oxyfuel calcination temperature range is 920 °C to 940 °C ( for the tests with fuel addition)

- Temperature established for entrained flow tests is higher than equilibrium temperature (air: 800 °C and oxyfuel: 880 °C)

- The raw meal particles itself do not show higher tendency of sintering or increased deposition tendency at oxyfuel calcination temperatures

The reference oxyfuel atmosphere for all the oxyfuel calcination test results reported above contains 80 vol.-% dry $CO_2$. It represents the ideally targeted oxyfuel calciner atmosphere. The temperature for oxyfuel calcination was in the range of 920 °C-940 °C, when fuel was introduced together with raw meal. The oxyfuel calcination temperature is significantly higher than the operating temperature of existing industrial calciners.

One of the issues with retrofitting existing air calciners to oxyfuel operation is the required temperature rise for oxyfuel mode to achieve similar degrees of calcination. The maximum temperatures in existing calciners are reported to be in the range 880 °C - 900 °C to avoid operational problems.

In the industrial calcination process the raw meal is preheated before entering the entrained calciner. The raw meal preheating occurs in cyclones (at different stages) and temperatures up to 750 °C are reached before entering the calciner. It is reported that up to 20 % of the raw meal is already calcined during the preheating stage. It should be mentioned that, part of calcined material which is found at this level comes from the calciner, due to low separation efficiency of cyclones. Considering the decomposition temperature of $CaCO_3$ in air case (~800 °C), the calciner mostly

has to provide the energy requirement to proceed the endothermic reaction of $CaCO_3$ decomposition. The fuel combustion inside the calciner provides that energy. Once the temperature threshold is reached, the decomposition starts and the calcination reaction is completed within seconds.

Another issue will be the formation of sticky compounds caused by fuel derived impurities. The concentration of these impurities is increased by the existence of sulfur and alkali cycles between preheater, calciner and kiln. Due to lower flue gas volume flows in oxyfuel operation these concentrations will be even higher. So it might prove impossible to increase the calciner temperature without risking operational problems due to deposit formation. A possible solution could be a purge of sulfur and alkali rich flue gas. Additionally, the practical level of $CO_2$ achieved inside the calciner when existing air calciners are retrofitted to operate in oxyfuel mode might not be as high as the targeted reference case. This might be an issue to be considered individually as in some cases the partial oxyfuel operation might be the more attractive retrofit option.

Further research and development work should be focused on the aforementioned issues and be extended to pilot scale trials in real calciner (hardware) configurations and the modeling studies for retrofitting options for preheating cyclones. To minimize the impact of burning fuel particles in an oxyfuel calciner even the fuel supply into the calciner should be reevaluated for oxyfuel conditions.

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# APPENDIX

## A    APPENDIX A

### A.1    Test Scenarios

Figure 16 shows different entrained calcination test scenarios conducted in the modified facility. After conducting the tests related to each scenario, the results were evaluated. The basic aim of updating the test scenarios was to establish the reference calcination scenario with comparable degree of calcination (≥90%).
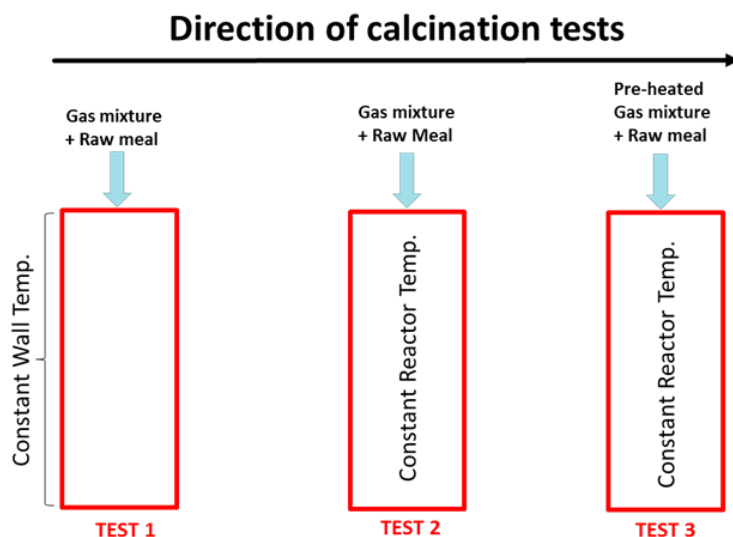


Figure 16: Entrained calcination test scenarios

Test 1 was performed at constant set wall temperature. The major tests conducted under test scenario 1 are listed Table 13.

Table 13: Major entrained calcination tests (TEST 1)

| AF (Air Case) | | | Oxy Case (OF) | | | |
|---|---|---|---|---|---|---|
| Gas mixture [$m^3$(STP)/h] | Wall Temperature [°C] | Test | Gas mixture [$m^3$(STP)/h] | Wall Temperature [°C] | Test | Comment |
| 7 | 950°C | 7AF-950°C | 7 | 950°C | 7OF-950°C | Each test were conduction for different raw meal feeding 1.9-0.3 kg/h |
| | | | 10 | 950°C | 10OF-950°C | |
| 7 | 1000°C | 7AF-1000°C | 7 | 1000°C | 7OF-1000°C | |

These were the preliminary tests conducted to check the suitability of the test setup and sampling system. These preliminary tests were conducted with pure limestone. The achieved degrees of

calcination during these tests were poor. After careful evaluation following conclusions were made:

- The actual temperature inside the reactor is lower than the set wall temperature.

- There is a significant temperature difference between air and oxyfuel mode, despite of similar set wall temperature.

These commission tests were the first tests after the modification of the test facility and sampling system. The main aim was to check the suitability of the setup. Additionally, the relation between set wall temperature and reactor centerline temperature for both air and oxyfuel case as well as the influence of raw meal feed rate was carefully evaluated.

These tests prevail that for a constant set wall temperature a temperature profile is established inside the reactor. Following lessons were learnt from the preliminary tests:

- For the same set wall temperature the temperature measured inside the reactor is lower for oxyfuel gas composition in comparison to air gas composition (see, Figure 17)

- With the same gas composition, changing the total gas flow injected into the reactor influences the temperature measured inside the reactor (see, Figure 17)

- The tested raw meal feeding rate range (0.3 to 1.9 kg/h) do not show significant impact on temperature inside the reactor.(see, Figure 18)
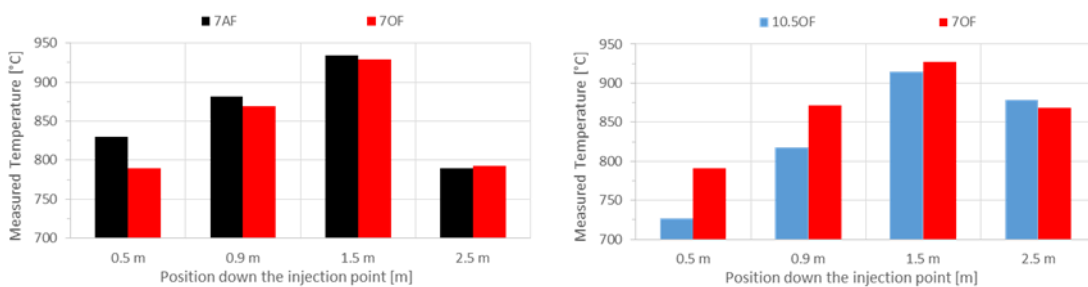


Figure 17: Temperature measured at different location with constant set wall temperature of 950°C; left showing influence of air (7AF) and oxy atmosphere (7OF), right showing influence of different gas flow 10.5 m$^3$(STP)/h oxy atmosphere (10.5 OF) and 7 m$^3$(STP)/h oxy atmosphere (7OF)
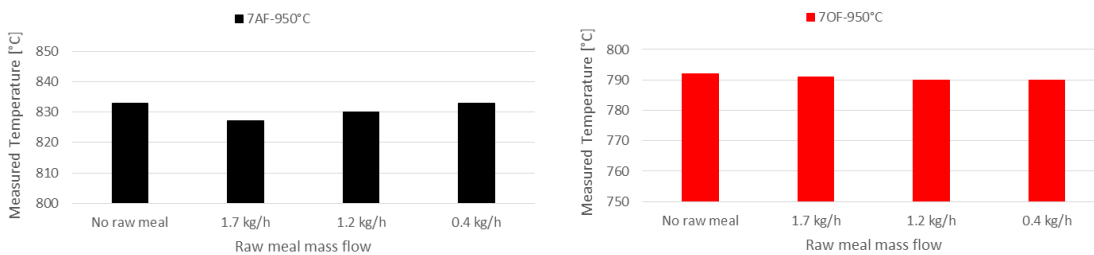


Figure 18: Temperature measured at 0.5m down the injection with different raw meal feed rate; left showing air case (AF-950°C) and right showing oxyfuel case (OF-950°C)

Test 2 was performed at a constant reactor temperature. The reactor temperature refers to the measured temperature along the reactor centerline. It is measured by thermocouples at 5 different positions, namely 0.5 m, 1.0 m, 1.5 m, 2.0 m and 2.5 m down the raw meal injection point. The reactor temperature for each test condition was established for given gas flow and atmosphere to ensure that the temperature is constant along the total length of the reactor. For doing so the heating zones (T1-T2-T3-T4-T5) were individually adjusted. For instant, to establish the uniform temperature of 910 °C throughout the reactor length with a total gas flow of 10.5 Nm$^3$/h (oxyfuel composition) the set wall temperature for the different heating zones (T1-T5) was 1030 °C-930 °C.  The major tests conducted under test scenario 2 are listed in Table 14.

Table 14: Major entrained calcination tests (TEST 2: No pre-heating)

| Air Calcination (AF) | | | Oxyfuel calcination (OF) | | |
|---|---|---|---|---|---|
| Gas mixture [m$^3$(STP)/h] | Reactor Temperature [°C] | Pre-heating | Gas mixture [m$^3$(STP)/h] | Reactor Temperature [°C] | Test |
| 10,5 | 880°C | 10,5AF-880°C | 10,5 | 910°C | 10,5OF-910°C |
| 10,5 | 885°C | 10,5AF-885°C | 10,5 | 935°C | 10,5OF-935°C |
| 10,5 | 895°C | 10,5AF-895°C | 10,5 | 950°C | 10,5OF-950°C |
| 10,5 | 905°C | 10,5AF-905°C | | | |

Test 3 included the preheating of the gas mixture and raw meal before injection into the reactor. All other conditions where similar to test scenario 2. Owing to the capability of the test facility the gas mixture was preheated up to 550 °C before entering the reactor. Two different raw meal preheating temperatures were achieved, 150 °C and 400 °C. It should be noted that the temperature inside the raw meal transport line was measured before entering the reactor. The heat to the raw meal particles in the transport line was supplied by heating the raw meal carrier air (650°C before it comes in contact with the raw meal) and by externally heating the transport line itself. The transport line was insulated to avoid heat losses to the environment. The major tests conducted under test scenario 3 are listed in Table 15 and Table 16.

Table 15: Major entrained calcination tests (TEST 3: With pre-heating, Gas mixture: 550°C and Raw meal: 150°C)

| Air Calcination (AF) | | | Oxyfuel calcination (OF) | | |
|---|---|---|---|---|---|
| Gas mixture [m$^3$(STP)/h] | Reactor Temperature [°C] | Test | Gas mixture [m$^3$(STP)/h] | Reactor Temperature [°C] | Test |
| 10 | 790°C | 10AF-790°C | 10 | 860°C | 10OF-860°C |
| 10 | 800°C | 10AF-800°C | 10 | 880°C | 10OF-880°C |
| 10 | 860°C | 10AF-860°C | 10 | 900°C | 10OF-900°C |
| 10 | 880°C | 10AF-880°C | 10 | 920°C | 10OF-920°C |
| 10 | 900°C | 10AF-900°C | 10 | 940°C | 10OF-940°C |
| | | | 10 | 960°C | 10OF-960°C |

Table 16: Major entrained calcination tests (Test 3: With preheating, Gas mixture: 550°C and Raw meal: 400°C)

| OxyFuel Calcination (OF) | | |
|---|---|---|
| Gas mixture [m³(STP)/h] | Reactor Temperature [°C] | Test |
| 10 | 920°C | 10OF-920°C |
| 7 | 920°C | 7OF-920°C |
| 5 | 920°C | 5OF-920°C |
| 10 | 940°C | 10OF-940°C |
| 9 | 940°C | 9OF-940°C |
| 7 | 940°C | 7OF-940°C |
| 5 | 940°C | 5OF-940°C |
| 10 | 950°C | 10OF-950°C |
| 9 | 950°C | 9OF-950°C |
| 7 | 950°C | 7OF-950°C |
| 5 | 950°C | 5OF-950°C |
| 10 | 960°C | 10OF-960°C |
| Air Calcination (AF) | | |
| 10 | 880°C | 10AF-880°C |
| 10 | 900°C | 10AF-900°C |

## A.2 Evaluation of degree of calcination

- From gas (CO2) measurement

The carbon dioxide concentration [vol%] is continually registered by the gas analyzer at the end of the reaction zone. In order to determine the degree of calcination, following formula is applied:

$$\text{Calcination[\%]} = \left(\frac{Meas \ \Delta CO_2}{Max \ \Delta CO_2}\right) * 100$$

Where,

Meas $\Delta CO_2$ is the measured difference in the $CO_2$ concentration, i.e. concentration of $CO_2$ with raw meal feeding minus initial $CO_2$ concentration without feeding (see, Figure 19).

Max $\Delta CO_2$ is the calculated maximum difference in $CO_2$ concentration, i.e. maximum amount of $CO_2$ that could be released for given raw meal feeding rate minus initial $CO_2$ concentration without raw meal feeding. The maximum $CO_2$ concentration is calculated as follows.

$$Max \ CO_2[\text{vol\%}] = \frac{\dot{V}_{CO_2}^g + \left(\frac{x_{CO_2}^{raw \ meal} \cdot \dot{M}_{raw \ meal} \cdot \tilde{V}_{CO_2}}{\tilde{M}_{CO_2}}\right)}{\dot{V}_{tot}^g}$$

Where $\dot{V}_{CO_2}^g$ is the volume flow of $CO_2$ in the gas mixture $\left[\frac{m^3}{h}\right]$

$x_{CO_2}^{raw \ meal}$ is the mass fraction of carbon dioxide in the raw meal [$wt.-\%$]

$\dot{M}_{raw\ meal}$ is the raw meal feeding rate $\left[\frac{g}{h}\right]$

$\tilde{V}_{CO_2}$ is the $CO_2$ molar volume $\left[\frac{m^3}{mol}\right]$

$\widetilde{M}_{CO_2}$ is the $CO_2$ molecular weight $\left[\frac{g}{mol}\right]$

$\dot{V}_{tot}^{g}$ is the total volume flow of gas mixture $\left[\frac{m^3}{h}\right]$
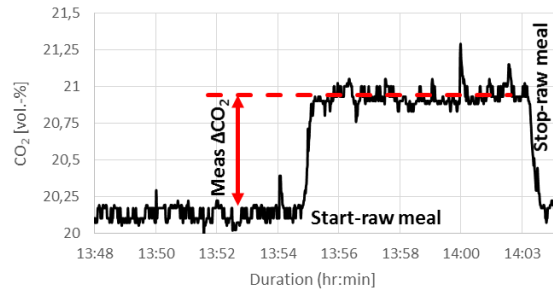


*Figure 19: Meas ΔCO₂ during calcination test (example case from air calcination tests)*

- From solid sample

The calcined solid samples are collected on a filter in addition to gas measurements. In order to determine the degree of calcination using solid samples, the equation below is applied.

$$\text{Calcination} = 1 - \left(\frac{x_{CO_2}^{sample} * \left(1 - x_{CO_2}^{raw\ meal}\right)}{\left(1 - x_{CO_2}^{sample}\right) * x_{CO_2}^{raw\ meal}}\right)$$

Where,

$x_{CO_2}^{raw\ meal}$ is the mass fraction of carbon dioxide in the raw meal $[-]$

$x_{CO_2}^{sample}$ is the mass fraction of carbon dioxide in the calcined sample $[-]$

Following approach was followed to determine the $CO_2$ content in the sample.

1. The solid sample is mixed with acid (HCl). Due to the reaction $CO_2$ is released from the sample. The resulting mass loss is used to derive the amount of $CO_2$ content (as wt.-%) in the sample.
   $CaCO_3 + 2HCl = CaCl_2 + CO_2 \uparrow + H_2O$
2. The solid sample is heated up to 950°C at $N_2$ atmosphere in a TGA. The resulting mass loss (620°C-950°C) is used to derive the amount of $CO_2$ content (as wt.-%).
3. The solid sample is heated at 950°C in $O_2$ atmosphere. The amount of $CO_2$ released form the sample is measured by gas analyzer (IR) and in turn used to evaluate the $CO_2$ content ( as wt.-%)

The calcination degrees resulting from the different methods are compared to evaluate the differences among the analyses. For air calcination the results from gas measurements give a satisfactory comparison with the evaluation made from solid sample analysis. The difference in $CO_2$ concentration could be clearly observed during air calcination tests due to large differences. For example, in air calcination tests with raw meal feed of 1 kg/h and total gas mixture of 10.5 m³/h in a gas atmosphere of 20 vol% $CO_2$ the maximum $CO_2$ reaches 21.29 vol% when all $CO_2$ in the raw meal is released. This gives a Max ΔCO₂ of 1.29 %. This value greatly exceeds

the measurement inaccuracy of the used $CO_2$ analyzer and the difference could be easily observed and evaluated.

On the other hand during oxyfuel calcination tests, with raw meal feed of 1 kg/h and total gas atmosphere of 10.5 m³/h in a gas atmosphere of 80 vol% $CO_2$, the maximum $CO_2$ reaches 80.32 vol% when all $CO_2$ in the raw meal is released. This gives a Max $\Delta CO_2$ of 0.32 %. This value is in the range of measurement inaccuracy of the used $CO_2$ analyzer and therefore the difference is hard to observe and evaluate. Moreover, the fluctuation of registered $CO_2$ concentration is even higher than the expected Max $\Delta CO_2$. For this reason the evaluation from gas measurements was not used for the comparison between air calcination case and oxyfuel calcination case. The gas measurements were only used during the tests to indicate that the calcination proceeds or not, in the given test condition.

Similarly, the solid sample analysis using acid (HCl) is as well used only as an indicative method to quickly evaluate the extent of calcination during oxyfuel calcination tests. The calcination degree reported in the results section of this report comes from the solid analysis following the approaches 2 and/or 3.

The calcination degree derived from different approaches (approach 2 and 3) are compared for some selected samples (Figure 20). The $CO_2$ content varies slightly with the analysis method.
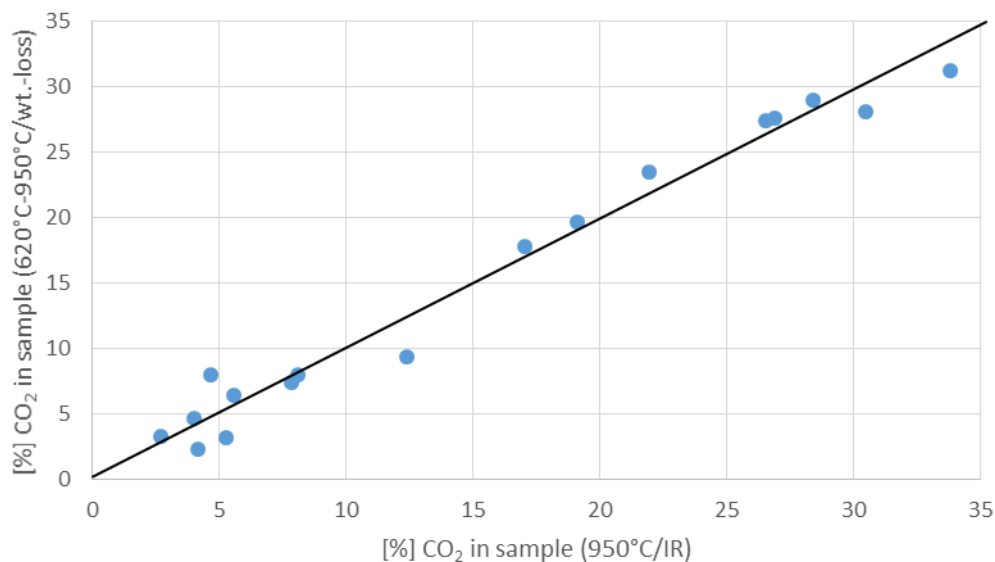


Figure 20: Comparison of sample analysis method

# B    APPENDIX B

Due to the measurement points of the calcination degree it is distinguishable that the reaction follows a logarithmic course. Therefore the logarithmic scale is assumed to apply for the extrapolation of compensating curves of the progress of the calcination reaction out of the measured values (see figure 17). The equation of these functions are then used to calculate the calcination rate as is shown in table 15.

PC: Pre-heater cyclones; EC: Entrained calciner
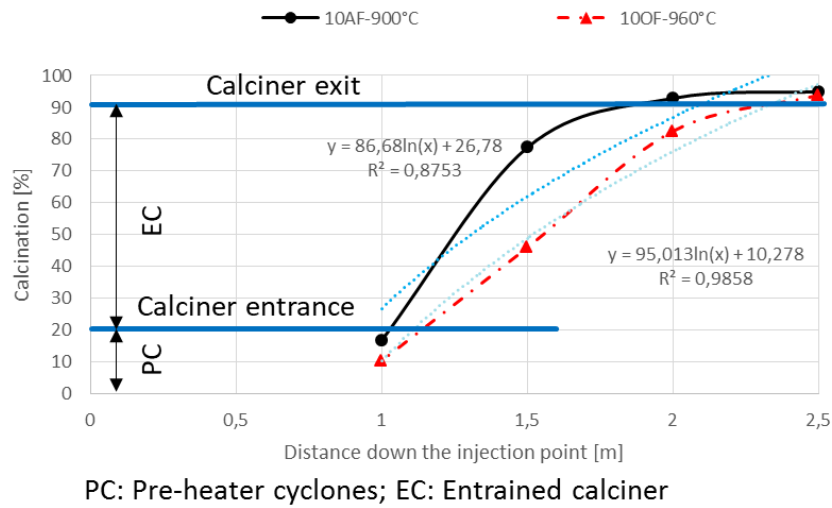
Figure 21: Calcination degree [%] at different distance down the injection point 10AF-900°C (air calcination) and 10OF-960°C (oxyfuel calcination)

Table 17: Calculated calcination degree [%] and calcination rate [%/s] for reference air case (10AF-900°C)

| | Calcination case | 10AF-900°C | | |
|---|---|---|---|---|
| | Velocity at 900°C [m/s] | 0.38 | | |
| Actual distance down the injection [m] | Effective distance [m] | Residence time [s] | AF calcination degree [%] | AF calcination rate [%/s] |
| 0.9 | 0 | 0.0 | 18 | |
| 1 | 0.1 | 0.3 | 27 | 35 |
| 1.1 | 0.2 | 0.5 | 35 | 31 |
| 1.2 | 0.3 | 0.8 | 43 | 29 |
| 1.3 | 0.4 | 1.1 | 50 | 26 |
| 1.4 | 0.5 | 1.3 | 56 | 24 |
| 1.5 | 0.6 | 1.6 | 62 | 23 |
| 1.6 | 0.7 | 1.8 | 68 | 21 |
| 1.7 | 0.8 | 2.1 | 73 | 20 |
| 1.8 | 0.9 | 2.4 | 78 | 19 |
| 1.9 | 1 | 2.6 | 82 | 18 |
| 2 | 1.1 | 2.9 | 87 | 17 |
| 2.1 | 1.2 | 3.2 | 91 | 16 |
| 2.2 | 1.3 | 3.4 | 95 | 15 |
| 2.3 | 1.4 | 3.7 | 99 | 15 |
| 2.4 | 1.5 | 3.9 | 100 | 4 |
| 2.5 | 1.6 | 4.2 | 100 | 0 |

Table 18: Calculated calcination degree [%] and calcination rate [%/s] for reference oxyfuel case (10OF-960°C)

| Actual distance down the injection [m] | Calcination case | 10OF-960°C | OF calcination degree [%] | OF calcination rate [%/s] |
|---|---|---|---|---|
| | Velocity at 960°C [m/s] | 0.40 | | |
| | Effective distance [m] | Residence time [s] | | |
| 1.1 | 0 | 0.0 | 19 | |
| 1.2 | 0.1 | 0.3 | 28 | 33 |
| 1.3 | 0.2 | 0.5 | 35 | 30 |
| 1.4 | 0.3 | 0.8 | 42 | 28 |
| 1.5 | 0.4 | 1.0 | 49 | 26 |
| 1.6 | 0.5 | 1.3 | 55 | 24 |
| 1.7 | 0.6 | 1.5 | 61 | 23 |
| 1.8 | 0.7 | 1.8 | 66 | 22 |
| 1.9 | 0.8 | 2.0 | 71 | 21 |
| 2 | 0.9 | 2.3 | 76 | 19 |
| 2.1 | 1 | 2.5 | 81 | 19 |
| 2.2 | 1.1 | 2.8 | 85 | 18 |
| 2.3 | 1.2 | 3.0 | 89 | 17 |
| 2.4 | 1.3 | 3.3 | 93 | 16 |
| 2.5 | 1.4 | 3.5 | 97 | 15 |
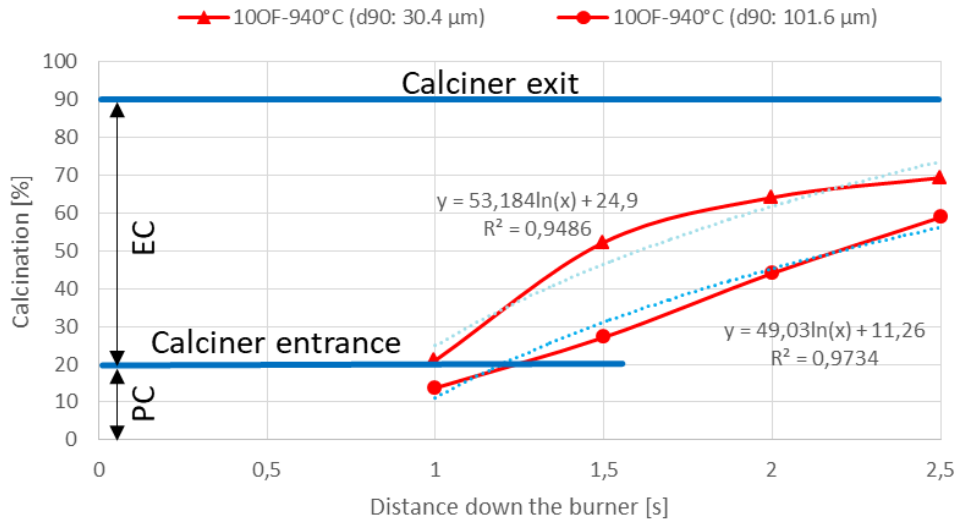


PC: Pre-heater cyclones; EC: Entrained calciner

Figure 22: Calcination degree [%] at different distance down the injection point 10OF-940°C (d90: 30.4) and 10OF-940°C (d90: 30.4)

Table 19: Calculated calcination degree [%] and calcination rate [%/] for oxyfuel case (10OF-940°C (d90:101.6 µm)

| Actual distance down the injection [m] | Calcination case | 10OF-940°C (d90: 101.6 µm) | | |
|---|---|---|---|---|
| | Velocity at 940°C [m/s] | 0.39 | | |
| | Effective length [m] | Residence time [s] | Calcination [%] | Calcination rate [%/s] |
| 1.2 | 0 | 0.00 | 20 | |
| 1.3 | 0.1 | 0.25 | 24 | 15 |
| 1.4 | 0.2 | 0.51 | 28 | 14 |
| 1.5 | 0.3 | 0.76 | 31 | 13 |
| 1.6 | 0.4 | 1.02 | 34 | 12 |
| 1.7 | 0.5 | 1.27 | 37 | 12 |
| 1.8 | 0.6 | 1.53 | 40 | 11 |
| 1.9 | 0.7 | 1.78 | 43 | 10 |
| 2 | 0.8 | 2.04 | 45 | 10 |
| 2.1 | 0.9 | 2.29 | 48 | 9 |
| 2.2 | 1 | 2.55 | 50 | 9 |
| 2.3 | 1.1 | 2.80 | 52 | 9 |
| 2.4 | 1.2 | 3.06 | 54 | 8 |
| 2.5 | 1.3 | 3.31 | 56 | 8 |

Table 20: Calculated calcination degree [%] and calcination rate [%/] for oxyfuel case (10OF-940°C (d90:30.4 μm)

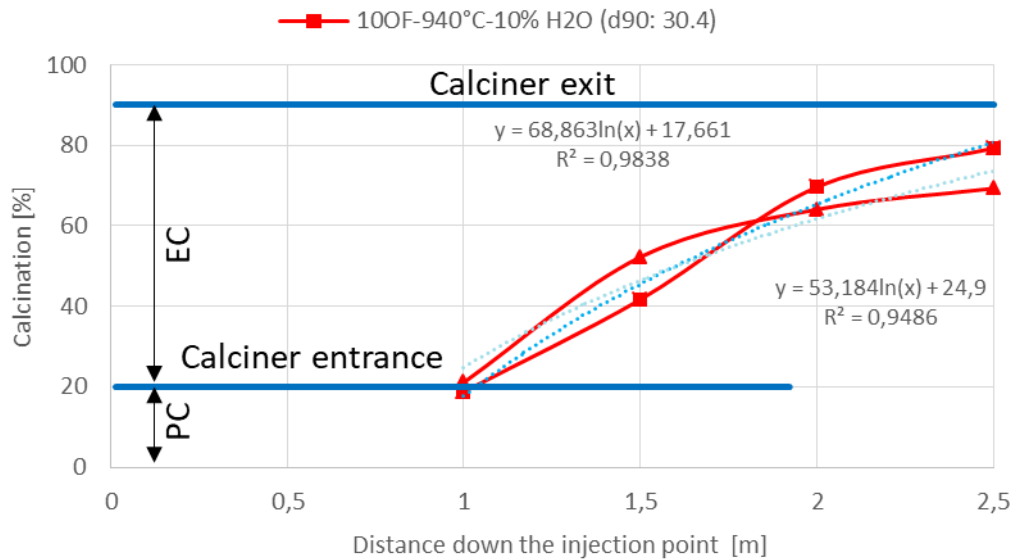| | Calcination case | 10OF-940°C (d90: 30.4 μm) | | |
|---|---|---|---|---|
| | Velocity at 940°C [m/s] | 0.39 | | |
| Actual distance down the injection [m] | Effective length [m] | Residence time [s] | Calcination [%] | Calcination rate [%/s] |
| 1 | 0 | 0.00 | 25 | |
| 1.1 | 0.1 | 0.25 | 30 | 20 |
| 1.2 | 0.2 | 0.51 | 35 | 18 |
| 1.3 | 0.3 | 0.76 | 39 | 17 |
| 1.4 | 0.4 | 1.02 | 43 | 15 |
| 1.5 | 0.5 | 1.27 | 46 | 14 |
| 1.6 | 0.6 | 1.53 | 50 | 13 |
| 1.7 | 0.7 | 1.78 | 53 | 13 |
| 1.8 | 0.8 | 2.04 | 56 | 12 |
| 1.9 | 0.9 | 2.29 | 59 | 11 |
| 2 | 1 | 2.55 | 62 | 11 |
| 2.1 | 1.1 | 2.80 | 64 | 10 |
| 2.2 | 1.2 | 3.06 | 67 | 10 |
| 2.3 | 1.3 | 3.31 | 69 | 9 |
| 2.4 | 1.4 | 3.56 | 71 | 9 |
| 2.5 | 1.5 | 3.82 | 74 | 9 |



Figure 23: Calcination degree [%] at different distance down the injection point 10OF-940°C-10%$H_2O$ (d90: 30.4) and 10OF-940°C (d90: 30.4)

Table 21: Calculated calcination degree [%] and calcination rate [%/] for oxyfuel case (10OF-940°C-10%H$_2$O (d90:30.4 µm)

| Calcination case | 10OF-940°C-10% H2O (d90: 30.4) | | | |
|---|---|---|---|---|
| | Velocity at 940°C [m/s] | 0.43 | | |
| Actual distance down the injection [m] | Effective length [m] | Residence time [s] | Calcination [%] | Calcination rate [%/s] |
| 1.1 | 0 | 0.00 | 24 | |
| 1.2 | 0.1 | 0.23 | 30 | 25 |
| 1.3 | 0.2 | 0.46 | 35 | 23 |
| 1.4 | 0.3 | 0.69 | 40 | 21 |
| 1.5 | 0.4 | 0.93 | 45 | 20 |
| 1.6 | 0.5 | 1.16 | 49 | 19 |
| 1.7 | 0.6 | 1.39 | 53 | 18 |
| 1.8 | 0.7 | 1.62 | 57 | 17 |
| 1.9 | 0.8 | 1.85 | 61 | 16 |
| 2 | 0.9 | 2.08 | 64 | 15 |
| 2.1 | 1 | 2.31 | 67 | 14 |
| 2.2 | 1.1 | 2.55 | 70 | 13 |
| 2.3 | 1.2 | 2.78 | 73 | 13 |
| 2.4 | 1.3 | 3.01 | 76 | 12 |
| 2.5 | 1.4 | 3.24 | 79 | 12 |

# C    APPENDIX C

Table 22 shows the major calcination tests with fuel addition. For each temperature case for the constant raw meal feed of 1 kg/h. different fuel amount was chosen. 0.025 kg/h. 0.05 kg/h and 0.1 kg/h.  The amount of fuel was so chosen to be within the range of fuel to raw meal ratio in industrial calciners. For the case 10OF-900°C the fuel feed was 0.1 kg/h. 0.2 kg/h and 0.3 kg/h.

Table 22: Major entrained calcination tests (with fuel addition)

| Air Calcination (AF) | | | Oxyfuel calcination (OF) | | |
|---|---|---|---|---|---|
| Gas mixture [m$^3$(STP)/h] | Reactor Temperature [°C] | Test | Gas mixture [m$^3$(STP)/h] | Reactor Temperature [°C] | Test |
| 10 | 860°C | 10AF-790°C | 10 | 900°C | 10OF-900°C |
| 10 | 880°C | 10AF-800°C | 10 | 920°C | 10OF-920°C |
| | | | 10 | 940°C | 10OF-940°C |

Two different kind of fuels (finely milled) were chosen for the test; fossil fuel. German lignite (GL) and non-fossil fuel torrified wood (TW). The composition and properties of fuel are shown in Table 23.

Table 23: Fuel used for calcination tests

| Fuel properties. as analyzed | German Lignite (GL) | Torrified wood pellets (TW) |
|---|---|---|
| Proximate analysis | | |
| Moisture [%] | 10.7 | 5.9 |
| Volatiles [%] | 46.6 | 67.8 |
| Ash [%] | 3.02 | 1.2 |
| Fix-C [%] | 39.7 | 25.15 |
| Ultimate analysis | | |
| C [%] | 58.4 | 52..6 |
| H [%] | 4.25 | 5.34 |
| N [%] | 0.702 | 0.745 |
| S [%] | 0.317 | 0.1 |
| Cl [%] | -- | 0.073 |
| O by diff. [%] | 22.61 | 34.09 |
| Lower heating value [MJ/Kg] | 22.2 | 19.4 |
| Particle size distribution | | |
| d10 | 6 µm | 12 µm |
| d50 | 30 µm | 53 µm |
| d90 | 150 µm | 204 µm |