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Abstract

Before proceeding to the design of a full oxyfuel cement pilot plant (TRL 7) the individual testing of key oxyfuel components (burner, calciner, cooler) has been executed based on the theoretical findings from the ECRA CCS project. Testing and demonstrating the oxyfuel calciner, clinker cooler and burner under industrially relevant conditions were undertaken in CEMCAP project (corresponding to reaching TRL 6). Due to the counter current flow in the clinker burning process and the recirculation of gases in the oxyfuel process, changes of the operational parameter in one process unit influence connected equipment units. An overall modelling of the oxyfuel operation is necessary. For this purpose the VDZ process model was adapted to the outcome of the CEMCAP prototype testing by including comprehensive data from the testing and restructuring the process modules. Based on the pilot testing results the calcination process of the raw material and the heat radiation profile in the kiln could be optimised. Moreover the amount of the false air ingress especially the air leakage from the cooler could be refined.
For further optimisation of the oxyfuel process model a parameter matrix was spanned. It included different operational modes, such as varying material and volume loads, combustion characteristics (flame length and shape), false air ingress and degree of heat exchange.

The simulation results of the optimised oxyfuel process model showed that by adaptation of the burner settings to the experimental results and by switching the oxygen supply from secondary to primary gas the heat transfer from the gas to the material could be enhanced. Thus, the heat transferred to the material in the sintering zone and the temperature profiles along the kiln are optimal to generate the required clinker phases. Furthermore it can be expected that the coating behaviour of the material in the kiln and the thermal load of the rotary kiln are similar in the optimised oxyfuel operation and the reference air case and therefore achieve an optimum operational mode. For the reference air case (optimum case) simulation results of a clinker burning process with best available techniques (BAT) and a clinker production of 3000 t/d was used. For equipment protection in the oxyfuel process with higher calcination temperatures the degree of calcination at the kiln inlet has been slightly decreased.

After the optimisation of the oxyfuel process model the waste heat recovery and the heat integration were evaluated with the help of an iterative procedure between the VDZ process model (PM) and the heat integration model. In order to evaluate the energy demand of the oxyfuel clinker burning process for different operation scenarios, the VDZ process model was applied for six different operation conditions, in which the false air ingress and the preheater stages were varied. Based on the process model results the process and energetic integration of the air separation unit (ASU) and CO_2 purification unit (CPU) and options for power generation by an Organic Rankine Cycle (ORC) were investigated by SINTEF.

The simulation results showed that the thermal energy demand of the clinker burning process rises by 0.8 – 1.3% per 2% of false air ingress mainly caused by the heating of the additional air. Simultaneously the specific power consumption of the CPU increases by 2.7 – 3.5% per 2% of false air ingress in the considered range of 4.6 – 8.1% due to the dilution of the flue gas by air. As the electrical energy demand for the CPU is rising exponentially with increasing false air ingress, the maximum acceptable level of false air ingress is around 8%.
This shows that the requirement for regular maintenance is much higher for the oxyfuel clinker burning process than for the clinker burning process with air operation.

The influence of the number of preheater stages on the ORC power generation was evaluated. The simulation results showed that decreasing the number of preheater stages leads to higher energy consumption in the ASU and CPU. With the consideration of the increased energy consumptions of ASU and CPU the ORC efficiency with the additional fuel used in the case of 4 and 3 preheater stages is +5.6% and +15.2%. It is obvious that from energetic perspective reducing the number of preheater stages to increase the ORC performance is not productive.

The adaptation of the VDZ process model to the experimental results and the optimised oxyfuel process model simulation results showed that a retrofit of existing plants is possible. But in order to refine the experimental results and evaluations and for validation of the simulation results and conclusions, experiments at a full scale oxyfuel cement pilot plant (TRL7) will be necessary.

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1 INTRODUCTION

Climate protection is seen as one of the key issues on the international policy agenda. Following the Paris climate agreement 2015 all signatory states are facing the challenge of reducing their CO_2 emissions significantly, focusing on the major CO_2 sources in order to contribute to the reduction targets being worked out in many countries as well as on a global level [ECR-09].

CO_2 emissions from the cement industry contribute with 6-7% of global anthropogenic CO_2 emissions. Hence, a significant reduction in emissions from the cement industry is required for meeting the European and global greenhouse gas (GHG) emission targets. At the same time it is necessary to maintain industrial competitiveness of cement production in Europe. CO_2 generation is an inherent part of the cement production process, due to the calcination of its raw material, limestone. $CaCO_3$ is converted to CaO and CO_2 and about 60% of the CO_2 emissions from cement production are due to this conversion, whereas 40% come from the combustion of fuels to provide heat for the clinker production. There are currently no feasible methods to produce clinker and thus cement without releasing CO_2 from $CaCO_3$. The only viable option to significantly reduce GHG emissions from the cement industry is CO_2 Capture and Storage/Utilization (CCS/U).

Cement plants typically have a lifetime of 30-50 years. Thus, CO_2 capture technologies should also allow retrofitting to existing cement plants. Technologies developed for CO_2 capture from power plants (many of them at TRL7-8), will need significant adaptation to be retrofittable to cement plants due to different processes and product requirements. When considered for the cement sector, such capture technologies were typically at TRL 4-5 or lower. Therefore, the CEMCAP project has been developed for bringing CO_2 capture technologies for the cement industry to a higher TRL level and thus closer to deployment.

The CEMCAP project focused on investigations on oxyfuel and post-combustion technologies as CO_2 capture technologies for cement kilns. The research work was organized into 12 work packages, which included theoretical work such as process modelling and engineering studies, but also laboratory and pilot-testing investigations.

The present report summarizes the research activities which were carried out in work package 6 “oxyfuel modelling and optimisation”.

2 STATE OF THE ART

Early experiences in the cement industry with the handling of oxygen for combustion have been made especially in the US focusing on increasing production capacity. Furthermore trials have been carried out aiming at the increase of the substitution rate of low calorific alternative fuels [LAU-11]. However, oxygen enrichment has not been applied to concentrate and capture CO_2 emissions in the cement industry so far [ECR-12].

Over the past few years, basic research on CO_2 capture from cement plants by the use of the oxyfuel technology has been conducted within e.g. ECRA's CCS project and Lafarge's project on partial oxyfuel [ECR-09, ECR-12, IEA-13]. The ECRA project includes the concept development, small-scale laboratory tests and process modelling. Based on these results it is stated that with oxyfuel technology, the thermal energy demand for cement production remains nearly unchanged while the electrical energy demand is nearly doubled, mainly due to oxygen generation. Most work related to the thermal process equipment like burner, calciner and clinker cooler design has so far been theoretical (process modelling and/or CFD).

It has become evident in the ECRA CCS project that key oxyfuel components (burner, calciner, cooler) should be tested separately (corresponding to reaching TRL 6), before proceeding to the design of a full oxyfuel cement pilot plant (TRL 7). Furthermore in the ECRA CCS project a basic model, which had been designed and extensively validated in the past years [LOC-02, KLE-06] has been adapted to the oxyfuel technology. The process model includes the clinker production process itself, the raw material drying, waste heat recovery, waste gas recirculation and other auxiliaries [ECR-09/ECR-12]. This model structure has been prepared for the purpose of further application in the CEMCAP project by identifying the parameters to be adapted.

2.1 Oxyfuel technology

The oxyfuel technology for CO_2 capture relies on pure oxygen instead of ambient air for combustion. For this purpose nitrogen is removed by an air separation plant (ASU) from the air prior to being supplied to the kiln for the combustion process. After the oxyfuel combustion and calcination process the concentration of carbon dioxide in flue gas is increased significantly. Also, the theoretical flame temperature in the sintering zone rises compared to ambient-air-based combustion. To maintain an appropriate flame temperature, part of the CO_2 rich flue gas has to be recycled while the recirculation rate adjusts the oxygen concentration in the combustion air and the combustion temperature. The oxygen concentration in the combustion air becomes an additional degree of freedom, where the optimum level must not necessarily be 21 vol.%.

As a consequence of the CO_2 enriched atmosphere in the kiln system (exceeding minimum 70 vol.%) only a comparatively simple carbon dioxide purification is required for the CO_2 capture from the flue gas cycle. As part of carbon capture and storage technology the purified CO_2 stream is discharged to a compression facility and then delivered to a transport system.

The gas properties are different from those in conventional kiln operation with a corresponding impact on the clinker burning process. For example energy is shifted in the clinker production process from area, where it is needed to properly form clinker phases due to the different specific heat capacity and radiation coefficient when switching from a N_2 to CO_2 dominated kiln atmosphere. Moreover especially the calcination reaction (meaning the decomposition of $CaCO_3$

to CaO and CO_2) is strongly influenced by the surrounding CO_2 concentration. Thus the equilibrium temperature of the reaction is rising with increasing CO_2 partial pressure.

2.2 Oxyfuel Process Layout

Basically oxyfuel technology could be applied to the clinker burning process on different scopes, which are defined as follows:

- Partial oxyfuel technology includes only part of the clinker production process, namely calciner and preheater, where most of the CO_2 is captured corresponding to all CO_2 from calcination and from 60% of the fuel combustion. That way the capture rate is limited to a maximum of 70%.
- Full oxyfuel technology includes the whole clinker production process, thus all the components need to be adapted. But capture rate is theoretically up to 99%.

In ECRA's CCS project is has been concluded, that the effort for partial oxyfuel technology (especially a necessary intensive waste heat recovery system) is too high for capturing only part of the generated CO_2. Thus the specific CO_2 capture costs are even higher [ECR-12]. Moreover retrofitting this system to existing plants seems nearly as complex as for the full oxyfuel technology. Therefore the ECRA and CEMCAP projects focus on full oxyfuel technology.

The principal configuration of an oxyfuel cement plant leaves the conventional plant in most parts unchanged. The relevant changes to the clinker production process are illustrated in Figure 2-1. In terms of retrofitting an existing cement plant the initial geometry of the equipment rotary kiln, preheater tower and calciner is kept unchanged. For the required gas tightness under oxyfuel operation the sealings have to be optimised compared to conventional plant operation.

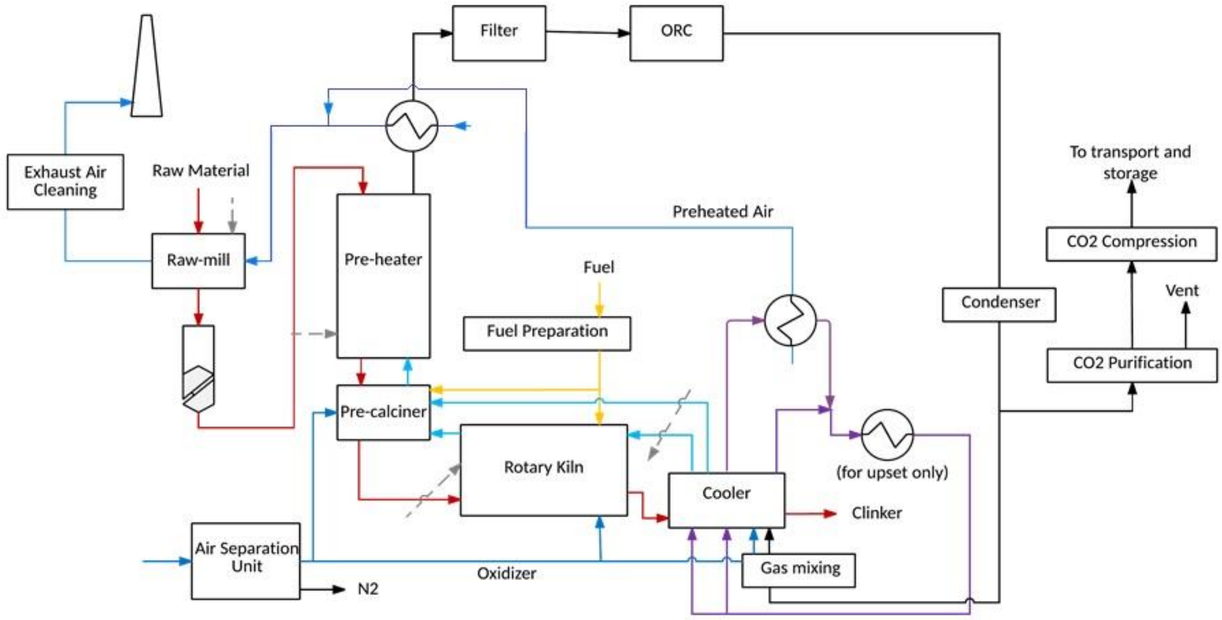

Figure 2-1 Scheme of the oxyfuel cement plant

The main additional installations required for the oxyfuel kiln are: (Figure 2-1)

- Rotary kiln burner for oxyfuel combustion, as described in WP 8.
- Oxyfuel clinker cooler (e.g. recirculating cooling), as described and tested in WP 9
- Exhaust gas recirculation system
- Gas-gas heat exchanger
- Condensing unit

- Air separation unit (ASU):
  A state-of-the-art cryogenic air separation unit (ASU) which produces 95 vol% O_2 is used in the process. The ASU has not been modelled as part of this work in CEMCAP. The energy consumption for oxygen production is taken to be 226 kWh/t_{O2} produced. Energy required for the dehydration process is taken to be 58.3 kJ/kg_{O2}. This heat is also assumed to be provided using an electric heater.

- CO_2 purification unit (CPU):
  A single stage flash, self-refrigerated CO_2 Processing Unit (CPU) suitable for pipeline transport of CO_2 is used. A schematic of the CPU is shown in Figure 2-2 below. The CO_2 stream after the condenser is compressed to specified pressure depending on the CO_2 capture ratio required. This stream is then dried using molecular sieves. This dry gas is cooled down to -50 °C in a multi-stream heat exchanger to liquefy the CO_2 and separate it from the other impurities such as nitrogen and oxygen. The CO_2 liquid is flashed to reduce the temperature to -54 °C. The liquid CO_2 (before flashing), the vapour CO_2 (after flashing) and the N_2 rich vent streams are used to cool down the feed gas to the CPU in the muti-stream heat exchanger. The minimum temperature difference between hot and cold composite curves in multi-stream heat exchanger is set to 3 °C. The vent stream is at a high pressure. This stream is heated to 180-200 °C and then expanded to recover work. This stream from the exit of the expander is heated and sent to the stack.

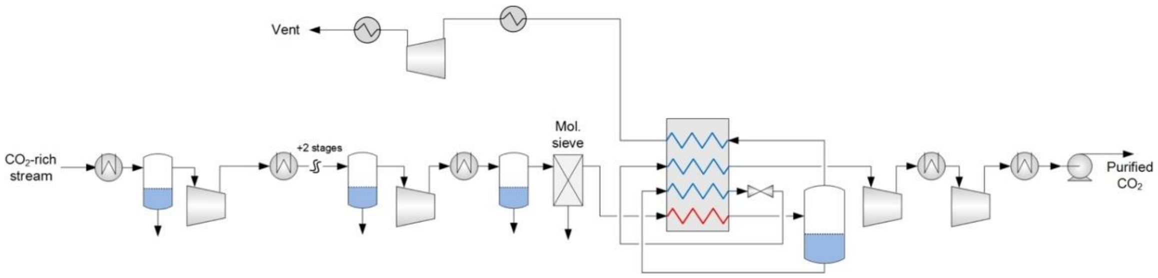

Figure 2-2 Schematic of single stage flash process CO_2 processing unit

The process can be optimised by varying the separator pressure, and keeping the pressure at the outlet of the throttle as high as possible without violating the minimum temperature difference in the multi-stream heat exchanger.

All process units' efficiencies are based on the deliverable D3.2 CEMCAP framework for comparative techno-economic analysis of CO_2 capture from cement plants. The heat requirement for the dehydration unit is assumed to be provided using an electric heater. This heat requirement is 4.6 $kWh_{th}/kg_{(H2O\ removed)}$.

3 INTEGRATION OF WP6 IN CEMCAP PROJECT

Testing and demonstrating key elements for application of the oxyfuel technology in cement plants were undertaken in CEMCAP project. Calciner, clinker cooler and burner technology for the oxyfuel process have been tested under industrially relevant conditions.

A burner designed by ThyssenKrupp (TKIS) for operating in oxyfuel conditions was investigated by the University of Stuttgart in CEMCAP work package 7 [GRA-18]. The major challenge of this campaign was that the operation conditions (e.g. ratio between primary air /secondary air, dust content in the secondary air) of a realistic cement plant and of the burner prototype test rig differ due to laboratory restrictions. A solution was found with the help of upscaling CFD simulations. The CFD simulations were validated with the experimental results and by this the flame characteristics of the burner for a realistic oxyfuel cement plant could be calculated.

A prerequisite of an appropriate operation of a pilot plant is the calcination of the raw material, which has been investigated in a 50 kWth test rig under dynamic industrial conditions by the University of Stuttgart in CEMCAP work package 8 [PAN-18, CIN-17] The main question, which was addressed, was the calcination process of the raw material for air and oxyfuel operation mode. The different operation modes were experimentally demonstrated.

The theoretical design of an oxyfuel clinker cooler has been tested by VDZ, IKN and HeildelbergCement in CEMCAP work package 9 [LIN17]. In order to evaluate the operating performance in terms of gas tightness, ingress of air and appropriate clinker cooling, a pilot-scale clinker cooler was designed, built, and operated on site of the HeidelbergCement plant in Hannover. Main questions related to the bed velocity, the mass and gas loads and false air ingress during the on-site operation of the pilot cooler.

Due to the counter current flow in the clinker burning process, e.g. changing the operational parameter in one process unit has influences on the connected equipment units. An overall modelling of the oxyfuel operation becomes necessary. For this purpose in CEMCAP work package 6 the VDZ process model was adapted to the outcome of the prototype testing (Figure 3-1) by applying results from the prototype testing and experimental work for adapting the process modules.

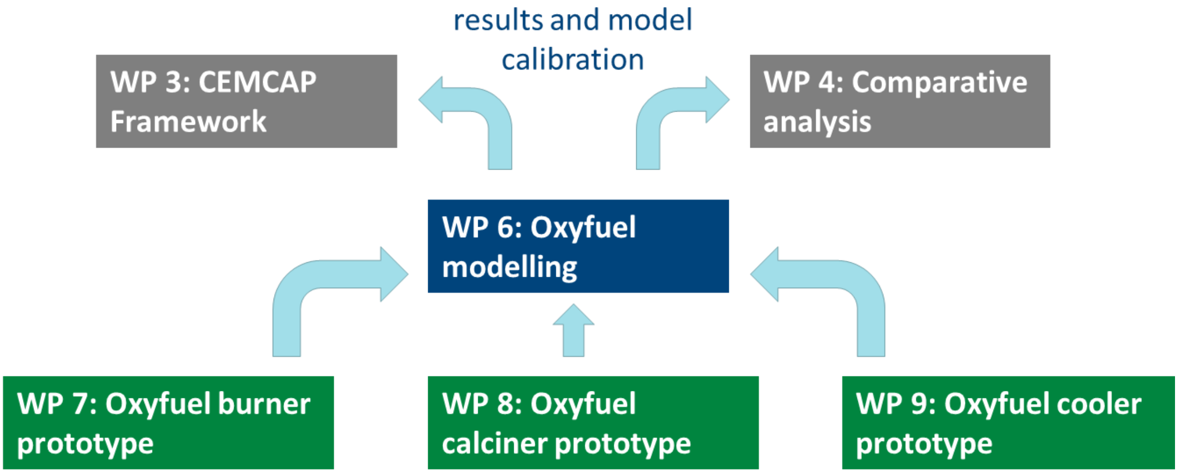

Figure 3-1 Integration of WP 6 in CEMCAP project

Based on the conducted prototype tests in WP7, WP8 and WP9 in WP6 oxyfuel modelling a parameter matrix was spanned including different operational modes, such as varying material and volume loads, combustion characteristics (flame length and shape), false air ingress and degree of heat exchange.
As a result, VDZ's oxyfuel process model provides information about the plant performance including the thermal energy demand, the clinker composition and available waste heat. Subsequently, this information was used in the SINTEF heat integration model. Within the process integration studies done at SINTEF the energetic integration of e.g. ASU and CPU based on PM simulation results have been simulated. The iterative procedure is shown below in Figure 3-2.

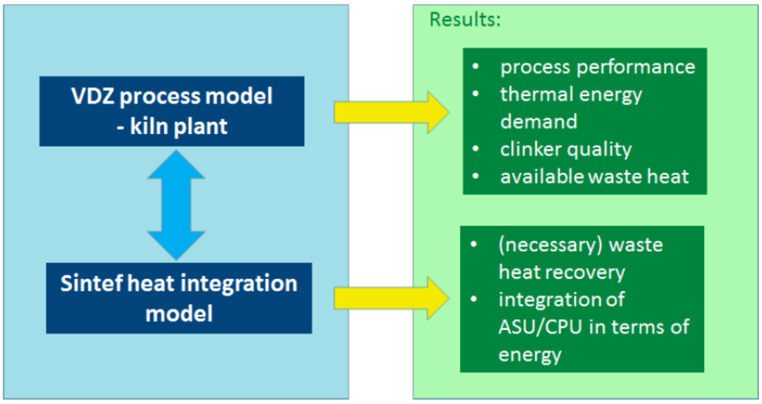

Figure 3-2: Interrelations of VDZ and SINTEF models

Different parameters for the operation conditions determine the performance of the process, such as recirculation rate, energy efficiency and product quality. Via process modelling and based on a parameter study the optimum operation condition for the oxyfuel clinker burning process have been determined (as presented in chapter 6).

Within the optimisation it was also considered that a minimal fuel energy demand does not imply a minimal overall energy demand. Options for power generation by waste heat have to be regarded for matching the electricity demand of the CPU/ASU. The identification of an optimal operational mode was a task of cooperation between SINTEF-ER and VDZ.

4 OXYFUEL PROCESS MODELLING

4.1 Mathematical modelling of cement clinker burning process

VDZ has developed a process engineering model, which is capable to realistically represent the clinker burning process. At its core it describes the process from the kiln meal feed to the outlet of the clinker from the cooler and is made up of individual models for the plant components preheater, calciner, bypass, rotary kiln and grate cooler. It is also possible to incorporate the plant sections of the external cycle, i.e. the evaporative cooler, raw grinding plant and dust collector. All the individual model sections can be linked mathematically with one another, which makes it possible to determine a steady-state condition for the entire clinker production process. Because of the modular structure the different plant circuits can be mathematically simulated comparatively easily and flexibly (Figure 4-1). The individual plant sections can also be defined geometrically so that different plant sizes can be simulated. Further inputs relate to the composition and mass flows of the raw materials and fuels as well as the volumetric flows of cooler inlet air, secondary air and, where appropriate, tertiary air.

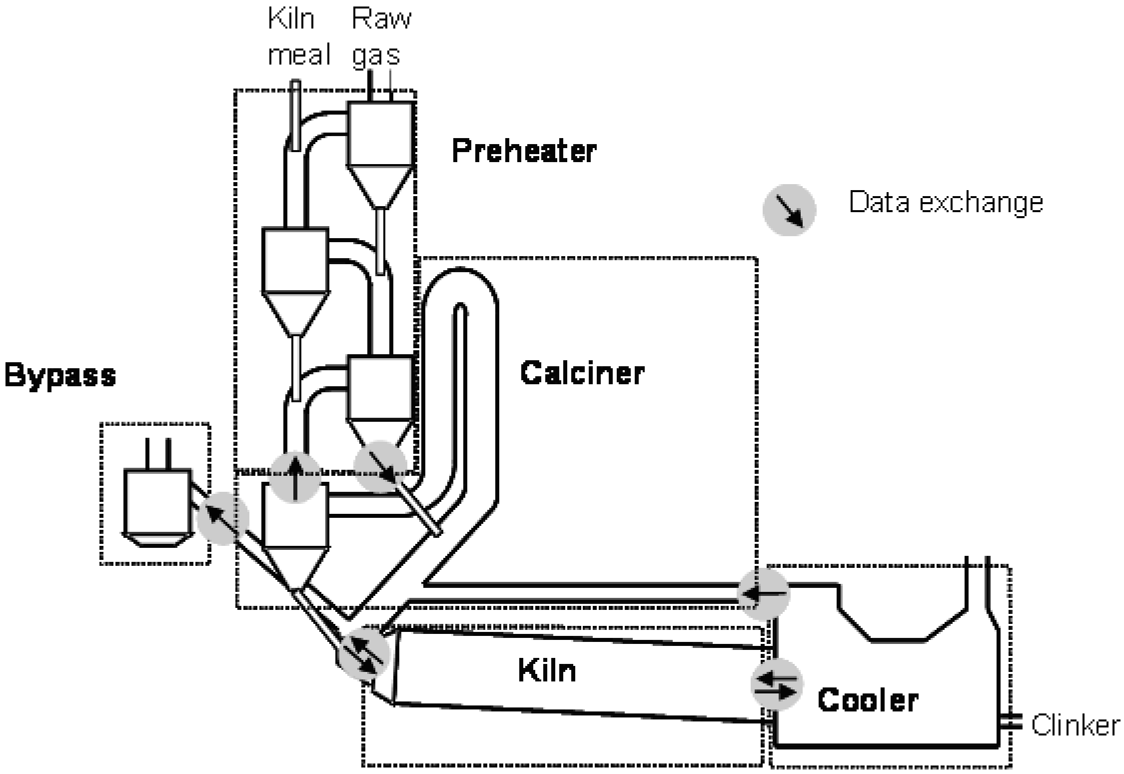

Figure 4-1: Model structure [LOC-02]

The calculations themselves cover the energy and material balances for the flows of fuel, dust and gas. Not only the combustion calculations for the fuels and the heat transfer but also the relevant chemical and mineralogical solid state reactions and the gas phase reactions as well as the gas-solids reactions are taken into account.

The calculations provide not only comprehensive process variables, such as mass and volume flows and their compositions, gas and solids temperatures and heat losses but also the specific energy requirement for burning the clinker.

Details about the basic model and model results are well described in [LOC-02] and [KLE-06]. In the following only essential model basics are described. Each model unit is defined by a series of general valid unit operations, like the one presented in Figure 4-2. Within the operator, material and gas phase are dispersed including temperature equalization, relevant reactions and element exchanges.

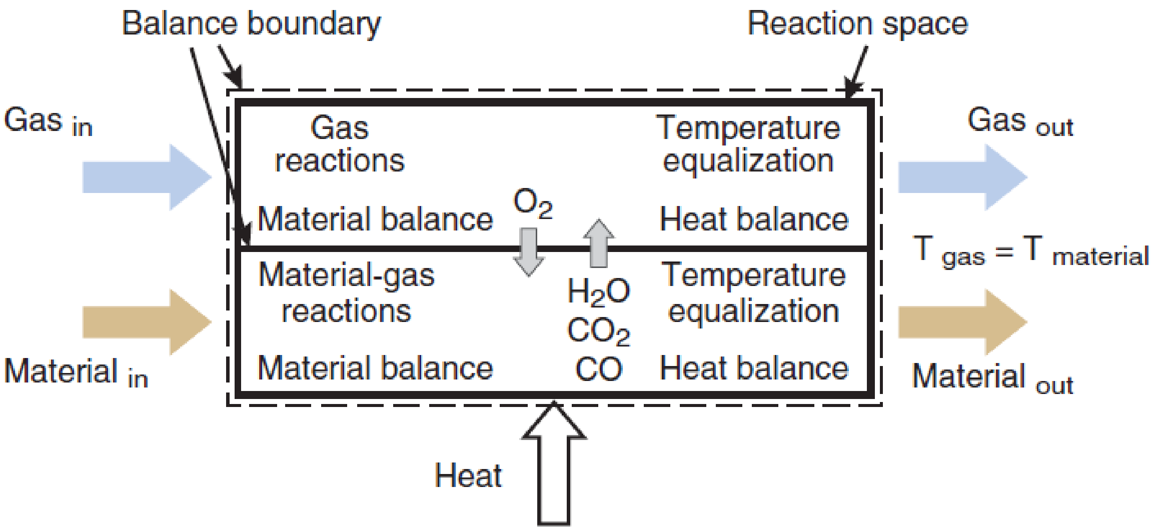

Figure 4-2: Unit operation: Dispersion of material and gas [LOC-02]

For the determination of the cyclone preheater the mix of material and gas for each cyclone stage is calculated by using different unit operations. The rotary kiln is subdivided into up to 50 segments, in which the material and energy balances are solved to create kiln profiles (Figure 4-3).

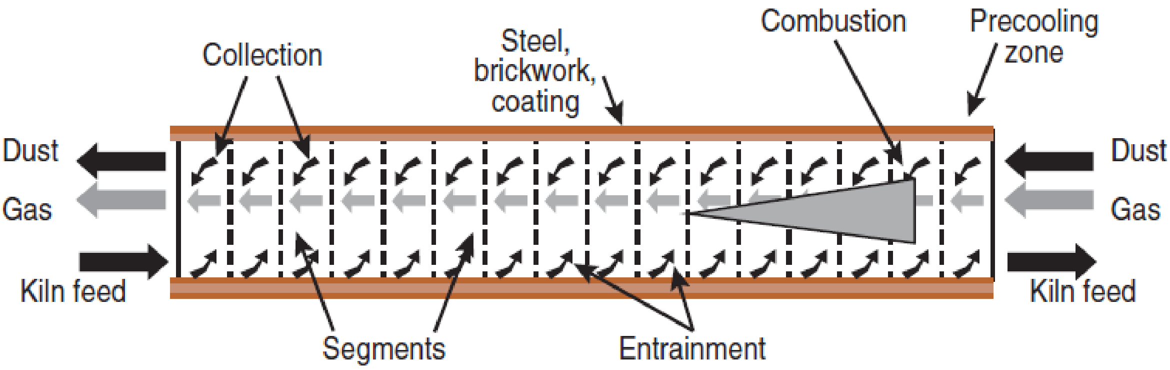

Figure 4-3: Subdivision of the kiln [LOC-02]

In each segment the exchange of energy (indirect or direct radiation/convection, wall losses) and mass, material/gas reactions, and entrainment of dust are solved (Figure 4-4). Depending on the used

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fuel the flame shape and length can be adapted. This influences the combustion gases along the kiln axis. Heat and combustion products are released in the respective elements.

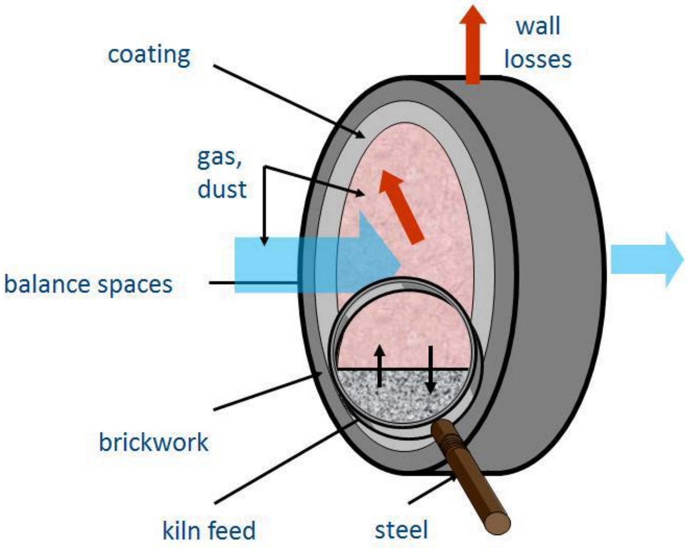

Figure 4-4: Calculation within one segment and result transfer [LOC-02]

To calculate the cooler the clinker bed is subdivided into segments alongside the cooler length and height. Each segment is streamed horizontally by clinker and vertically by cooling air (Figure 4-5). Energy and mass balances are solved for each segment, starting with known flow conditions at cooler entrance. Thereby the new conditions (temperature, composition etc.) of material and gas can be supplied to the subsequent segment.

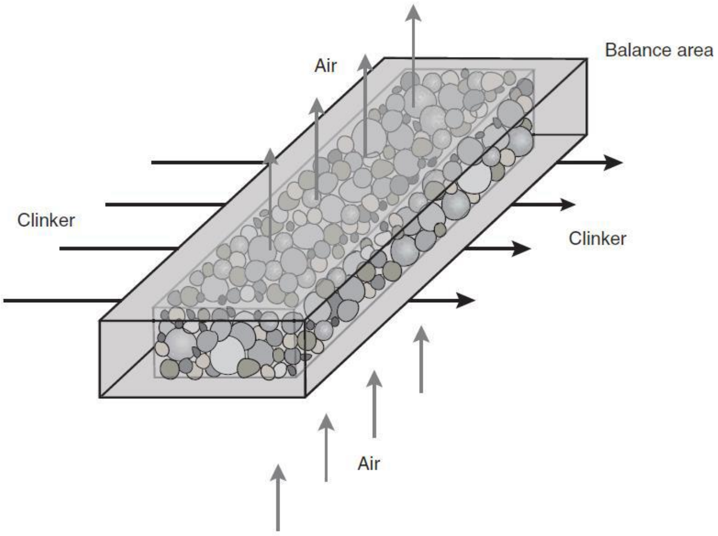

Figure 4-5: Subdivision of the clinker bed alongside the grate cooler [LOC-02]

4.2 Process simulation of a rotary cement kiln under oxyfuel conditions

The operation under oxyfuel conditions will influence the operation of all plant units. E.g. the heat transfer, the combustion, the capacity streams of material and gas as well as the clinker formation are affected due to the different gas properties like heat capacity, emissivity or density.

To optimise the modelling of the oxyfuel clinker burning operation, which was determined in the ECRA CCS project phase III, the CEMCAP experimental results from the different work packages (WP7, 8 and 9) were used as new input parameters. The required parameters from the respective WPs are shown in Figure 4-6 and listed in the following sections.

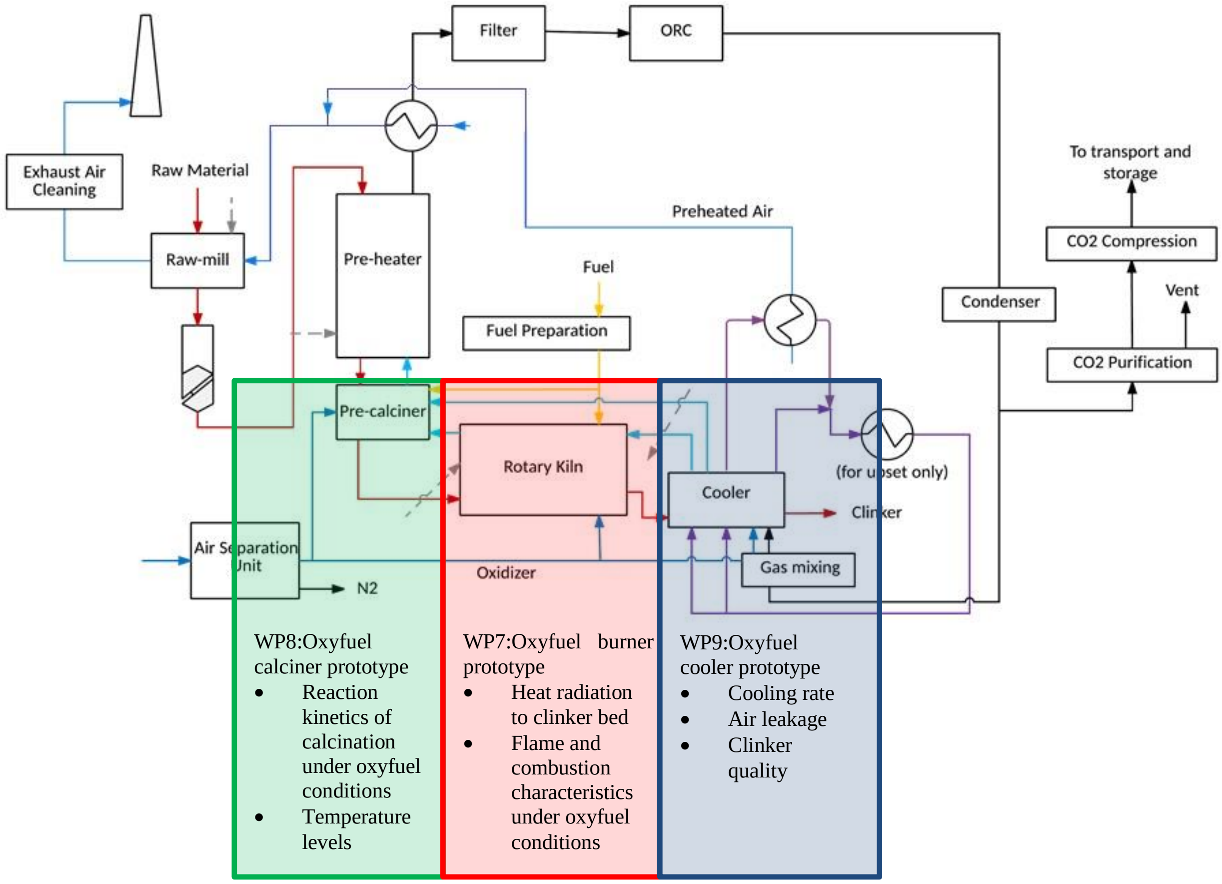

Figure 4-6: Refined parameters by experimental tests

4.3 Model adaptation: Oxyfuel burner technology (WP7)

Burning conditions, especially the gas and solid temperature profiles in the rotary kiln are the crucial factors for material conversion and therefore final product quality. In order to prove if an oxyfuel burner is able to reproduce similar heat transfer flux profiles along the kiln compared to conventional combustion with air, an oxyfuel prototype burner has been tested in the test facility of University of Stuttgart.

The input parameter from the oxyfuel burner tests (WP7) to the process modelling (WP6) are:

- Heat radiation to clinker bed
    - Optimised oxyfuel case with a heat radiation profile to the material similar to that in the reference case (air case)
- Flame and combustion characteristics under oxyfuel conditions
    - Flame length and flame shape in connection to optimised heat radiation

In order to overcome restrictions for the direct transfer of results originating from the test rig CFD simulations for upscaling were performed by SINTEF and an iterative collaboration between testing and modelling led to validated results at appropriate scale. The procedure for the data-exchange between the CFD-model (SINTEF) and the process model (VDZ) has been defined by VDZ, TKIS (ThyssenKrupp Industrial Solutions), SINTEF and IFK as shown in Figure 4-7.

The prototype testing provided validation data (such as gas radiation, temperature profile, fuel burnout) to SINTEF's CFD model. Based on CFD modelling under cement plant specific conditions relevant parameters for determining an optimised burner design and operation has been determined. The following procedure has been used:

- Set-up of the CFD model based on up-scaled industrial burner geometry
- Definition of suitable initial input data of industrial plant to start CFD modelling (ratio of primary to secondary gas, dust loads and properties, volume flows)
- Validation of the CFD model by WP7 experimental results
- Iterative information exchange (heat radiation, flame characteristics) between CFD and process modelling, as shown in Figure 4-7

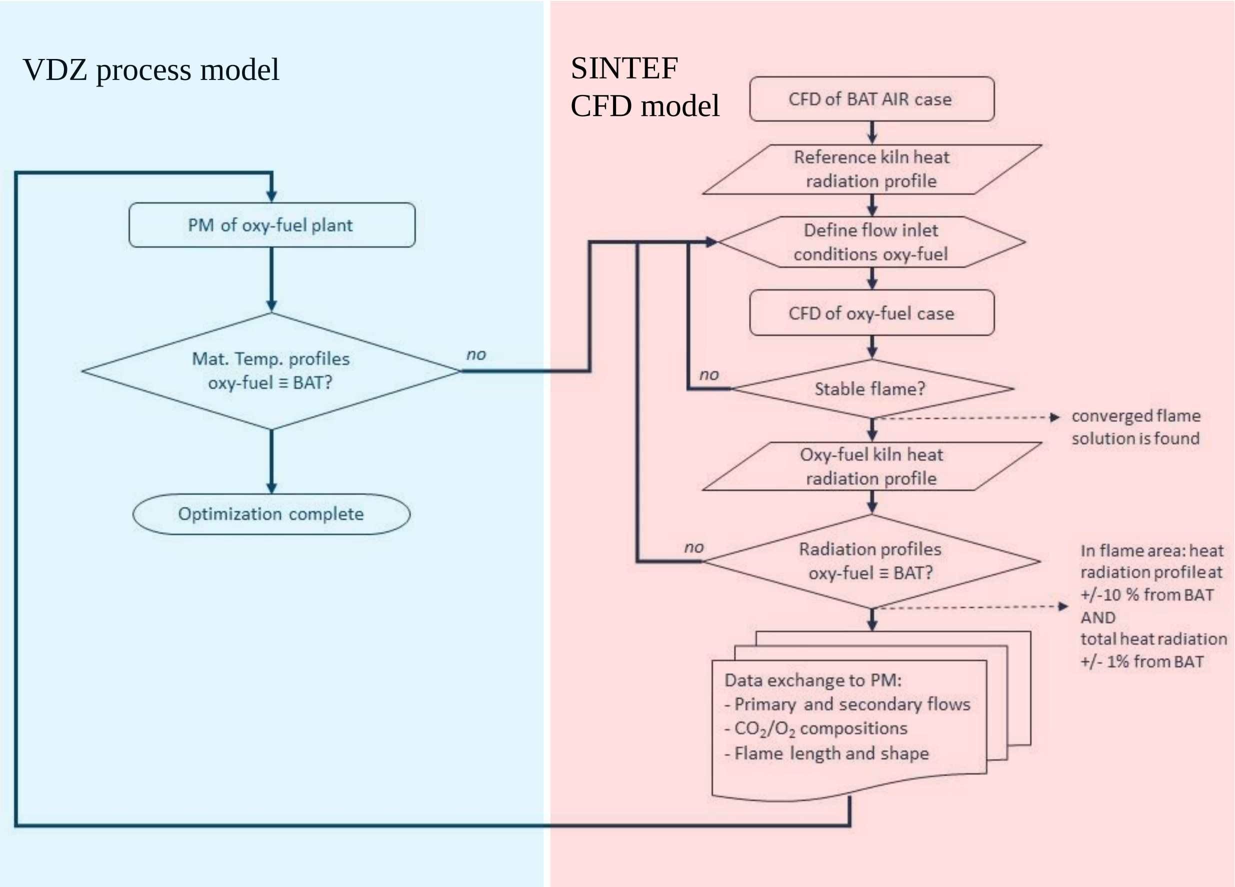

Figure 4-7: Methodology for process optimisation

Simulated heat radiation- and material temperature profile

Several CFD simulations have been performed to determine the reference BAT air case and various oxyfuel cases. The iterative procedure led to the set of input parameters (inlet flow rates, temperatures, and compositions, swirl angle) summarized in Table 4-1 for the optimised oxyfuel case. On this basis a flame in the rotary kiln is generated, which provides a heat radiation profile to the material similar to the reference case (BAT300) (Figure 4-8). The major difference to the reference air case (BAT3000) is the distribution of the oxygen between primary and secondary gas due to the different gas properties. While secondary gas is preheated by cooling down the hot clinker, primary gas is supplied by the burner for the purpose of fuel transport and flame shaping (swirl, axial gas). These results relate to WP7 report D7.3.

Table 4-1: Inlet properties used in the CFD simulations

		AIR-REF	OXYFUEL
Primary gas			
Volume flow	m^3_{stp}/h	5100	4500
Temperature	K	323	323
Composition			
N_2 or CO_2		N_2	CO_2
O_2%	vol.%	21	60
N_2 or CO_2%	vol.%	79	40
Swirl degree		20°	30°
Velocity	m/s	250	221
Carrier gas			
Volume flow	m^3_{stp}/h	4040	1050
Temperature	K	323	323
Composition			
N_2 or CO_2		N_2	CO_2
O_2%	vol.%	21	18
N_2 or CO_2%	vol.%	79	82
Velocity	m/s	38	10
Fuel			
type		coal	coal
mass flow	kg/s	1.47	1.47
stoichiometric O2 mass	gO_2/gfuel	2.07	2.07
Primary + Carrier + flame detector gas			
Volume flow	m^3_{stp}/h	9140	5550
Temperature	K	323	323
Composition			
N_2 or CO_2		N_2	CO_2
O_2%	vol.%	21	52.1
N_2 or CO_2%		79	47.9
O_2	m^3_{stp}/h	1919	2889
N_2 or CO_2	m^3_{stp}/h	7221	2661
available combustion O_2	gO_2/gfuel	0.5	0.8
Secondary gas			
Volume flow	m^3_{stp}/h	29090	28126
Temperature	K	1073	1273
Composition			
N_2 or CO_2		N_2	CO_2
O_2%	vol.%	21	20.8
N_2 or CO_2%	vol.%	79	79.2
Velocity	m/s	3.7	4.3
Flame length	m	17	16.8
Flame shape	m	Triangular	Triangular

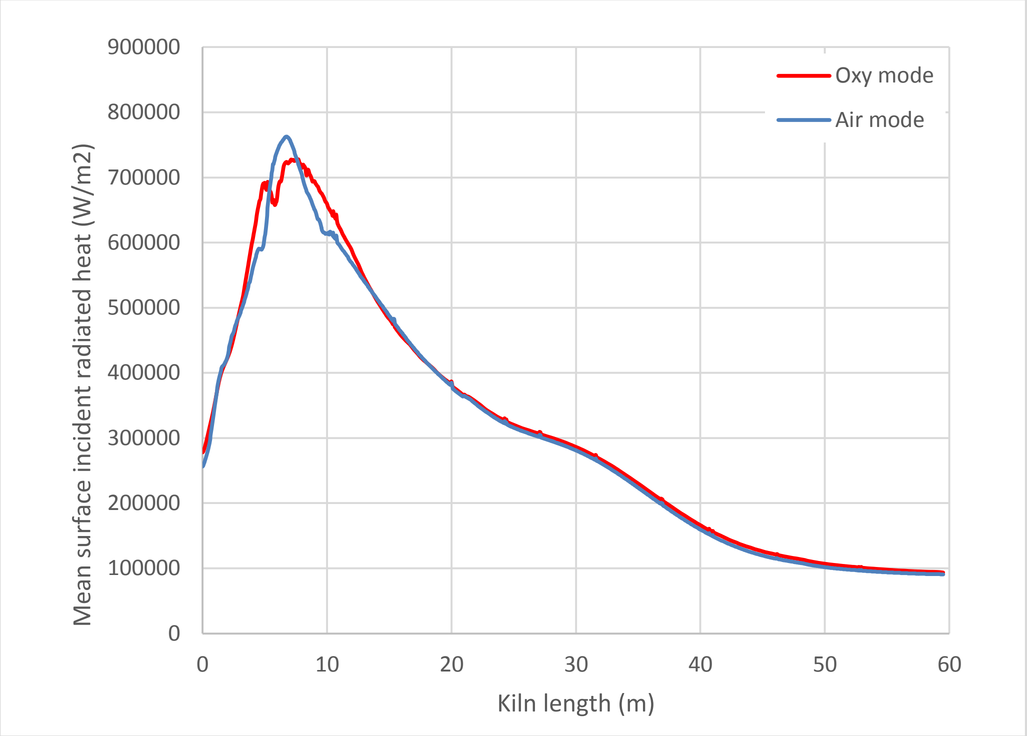

Figure 4-8: Heat radiation from gas to material for oxyfuel and air mode simulated by the CFD model

Table 4-2 shows the comparison of the assumed parameters based on theoretical considerations implemented in the VDZ process model [ECR-12] and the optimised parameters based on the experimental results during the CEMCAP project.

Table 4-2: Burner specifications elaborated during the CEMCAP project

Description	Assumed parameters	CEMCAP final results
Primary gas O_2 concentration [%]	35	52
Secondary gas O_2 concentration [%]	22	21
Primary gas volume flow [m^3_{stp}/h]	3,620	5,550
Secondary gas volume flow [m^3_{stp}/h]	36,787	28,126
Flame length [m]	18	16.8

To achieve similar heat radiation profiles of oxyfuel and reference air operation (BAT3000) the oxygen concentration in the primary gas in oxyfuel operation should be significantly higher than the theoretical assumption made in the VDZ process model [ECR-12]. In the (CEMCAP) simulated results the volume flow and the oxygen concentration of the secondary gas is lower than the assumed values [ECR-12]. This is due to the relatively high oxygen concentration in the primary gas, which was determined during the CEMCAP project for the optimisation of the flame characteristics and thus the heat transfer from gas to material. After the determination of the relevant parameters the VDZ process model was adapted to the burner specifications listed in Table 4-2.

4.4 Model adaptation: Calciner technology for oxyfuel process (WP8)

The calcination experiments were carried out in an electrically heated entrained flow reactor (Figure 4-9). The functionality of the reactor is similar to drop tube reactors. The ceramic tube was electrically heated (externally) to keep the desired temperature inside the reactor chamber. Furthermore the raw material/limestone was preheated before it was fed from the top of the reactor to the heating zone of the reactor. A gas mixture of N_2, CO_2, H_2O (vapour) and O_2 was fed together with the raw material/limestone to the reactor to simulate the air fired case atmosphere (20% CO_2) and the oxyfuel atmosphere (80% CO_2).

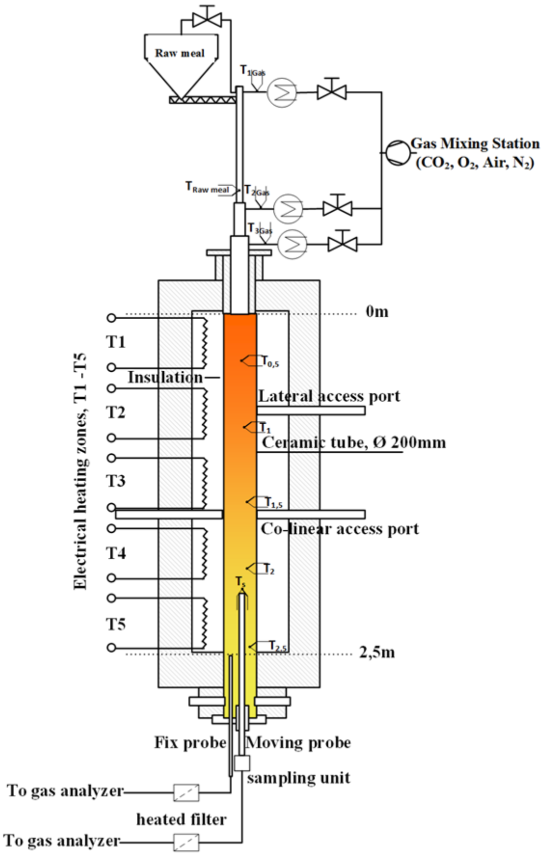

Figure 4-9: Schematic outline of calcination test facility at IFK

The input parameter from the calciner tests (WP8) to the process modelling (WP6) are:

- Calcination end and start temperature: Calcination end temperature refers to the temperature for 100% calcination. Calcination start temperature refers to the temperature at which the raw meal starts to release CO_2.
- Required residence time of the particles in the calciner (oxyfuel vs. air mode).

<u>Calcination start and end temperature</u>

In the first step the calcination start temperature has been determined by a thermal gravimetric analysis (TGA) of the raw meal sample in the relevant air and oxyfuel atmospheres. The TGA is capable to record very small changes in sample mass in dependence of temperature to mark the calcination start. The calcination start temperature, which was determined by the TGA analysis, is at 610°C for both cases (oxyfuel and air case).

To determine the calcination end temperature at 100% degree of calcination, various solid samples were heated up to different temperature levels and the remaining CO_2 content was analysed in order to determine the degree of calcination (Figure 4-10).

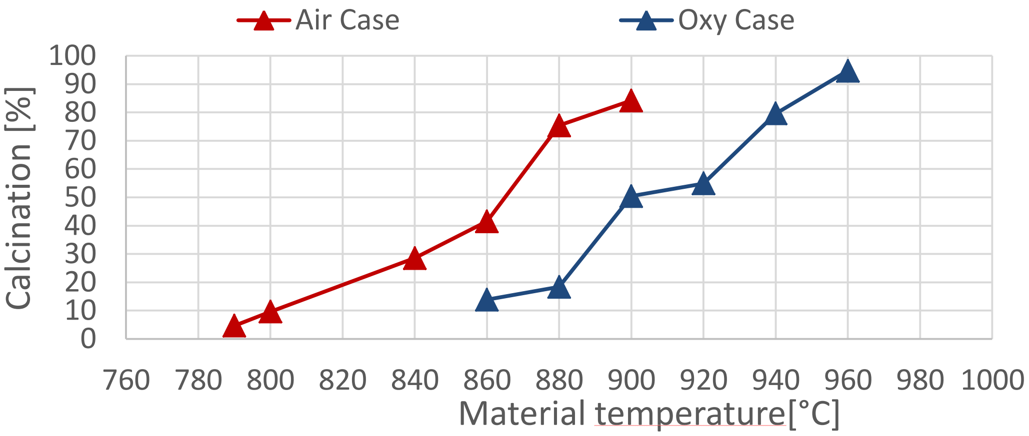

Figure 4-10: Calcination [%] derived from solid sample analysis

To identify the calcination end temperature i.e. (100% degree of calcination), an average trend of the reaction progress with temperature around 90% calcination has been extrapolated (Figure 4-11, see also WP8 report D8.3). The identified temperature shift of about +60 °C between the oxyfuel case (980 °C) and the air case (920 °C) was correctly reflected by the extrapolated calcination end temperatures. However, the absolute values for the calcination end temperature seemed very high compared to values reported in literature.

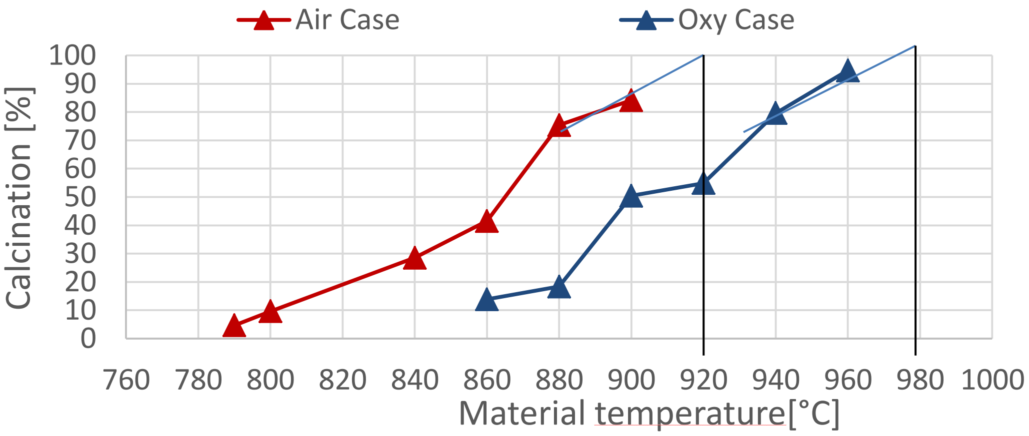

Figure 4-11: Extrapolation for the trend of raw material calcination

The discussion of the results indicated measurement errors caused by radiation bias (rough estimation of -30°C correction). Accordingly, the calcination end temperatures were corrected by this value to 890 °C for the air case and 950°C for the oxyfuel case. The following table shows the determined calcination start- and end temperature of the raw material.

Table 4-3: Calcination start- and end temperature for the oxyfuel and air model

	Air (20% CO_2)	Oxyfuel (80% CO_2)
Calcination start-temperature	610 °C	610 °C
Calcination end-temperature	890 °C	950 °C

As shown in Table 4-3 the calcination end temperature is shifted by 60 °C towards higher temperatures with increasing CO_2 concentration in the combustion gas.

From experimental campaigns, described in D 8.1, D 8.2 and summarized in D 8.3, it appears clearly that the calcination end temperature in oxyfuel mode will increase up to 940-960 °C. In calciners, fitted on existing kilns and operated in air mode, the gas temperature at the outlet is controlled continuously and kept around 870 °C (see fig. 3.3.1.3 in D 8.3). Considering that there is always a relatively small difference between the temperature of gas and solids, also in oxyfuel mode the temperature of the material will be probably around 920 °C. The small difference is due to the reaction of dissociation of limestone, which can be considered as a transition between two different phases.

The temperature of 920 °C in specific cases can be cause of unwanted coating in the calciner. Two possible solutions can be adopted in this case:

The first one relies on the flexibility of kiln operation. It is possible to reduce the calcination degree, reducing the typical amount of thermal energy supplied to the calciner from 60%, for instance, to 55% or even to 50%. In this case the reaction of limestone dissociation will be completed in the first few meters of the rotary kiln, what already happens in practice in air operation mode but just from a degree of calcination of 92-95% to 100%, while in case of oxyfuel operation mode it will be from 75-80% to 100%.

In case the first solution can’t be adopted because, for instance, the rotary kiln is very short (length to diameter ratio 10-11), it is necessary to implement a second solution by increase of the residence time in the calciner, as already mentioned at page 12 of the D8.3 report. This means to increase the calciner volume, what is frequently done also to improve the capacity of burning alternative fuels, like chopped tires and RDF. In a calciner with a higher volume the residence time of raw meal will be longer and the calcination reaction will be almost completed even at lower temperature.

Being almost impossible to reproduce the effects of all influencing parameters on cement kiln operations though mathematical and physical modelling, it is very important to verify the coherence of the trends. This analysis has been performed on the pilot scale in CEMCAP Workpackage 8 experiments. The experiments with raw meal and addition of fuel confirmed the calcination end temperature shift by 60 °C between air operation mode (890 °C) and oxyfuel operation mode (950 °C; see CEMCAP D8.3, Figure 3.3.1.2, TRL 6). Further demonstration will be required at the integrated plant scale (TRL 7 and 8). The typical flexibility of almost all kilns is most probably enough to compensate variations within the stated values of the degree of calcination and temperatures without jeopardizing the production levels and clinker quality.

After the adaptation of the VDZ process model to the burner specifications (chapter 4.3) the experimental results of the calcination process under oxyfuel conditions (calcination end temperature 950 °C) were implemented in the PM. The thermal energy input in the calciner and main burner was afterwards adapted to the new operation conditions to achieve a material temperature profile similar to the reference case (BAT3000).

The thermal energy input for the calcination process has to be increased in the oxyfuel case (calcination end temperature 950 °C). A part of the calcination is shifted to the kiln and the thermal energy input of the main burner has to be increased. After complete calcination, finally, the energy input and flame formation also has to be adjusted in order to achieve the required conditions for clinker phase formation (i.e. 1450 °C material temperature in the sintering zone).

Residence time

In order to investigate the impact of higher CO_2 concentrations on the required particle residence time additional tests have been executed in WP8 based on the previously determined calcination end temperatures (890 °C air case, 950 °C oxyfuel case, see Table 4-3). Different residence times have been realized by sampling at different location inside the reactor. The samples have been assessed in terms of degree of calcination achieved at different locations in the reactor but at constant temperature.

The experiments have shown that the residence time of 3 s in the calciner would be sufficient for the calcination of raw material in the oxyfuel- and air-case if the required calcination temperature is achieved by raw meal particles. Therefore the current model assumption of 3 s is a valid assumption.

4.5 Model adaptation: Oxyfuel clinker cooler prototype (WP9)

In order to prove the performance of an oxyfuel clinker cooler in terms of gas tightness and cooling performance prototype tests have been executed. The general concept of the oxyfuel clinker cooler prototype is shown in Figure 4-12.

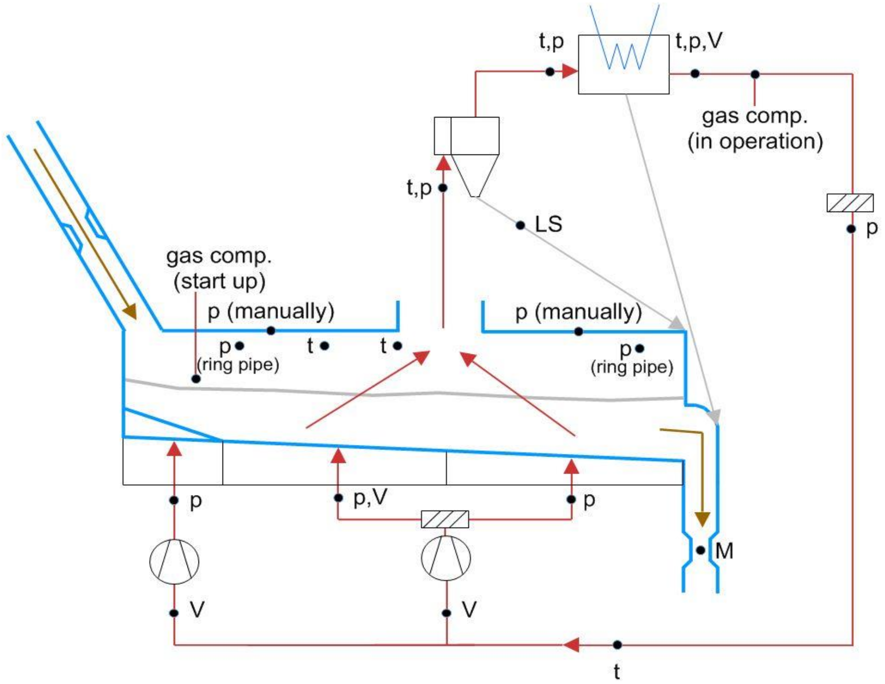

Figure 4-12: the Oxyfuel Cooler Prototype – Operation

A low percentage of hot clinker (approximately 3% of the usual clinker production of the main kiln line) has been extracted from the kiln hood of the main kiln line (HeidelbergCement plant in Hannover) and supplied into the oxyfuel cooler.

The oxyfuel clinker cooler prototype was operated with CO_2 rich gas and ambient air as cooling medium. The cooling medium was circulated in a closed loop: After passing through the clinker bed the heated gas was de-dusted in a cyclone and afterwards cooled down by a gas/air heat exchanger to approximately 100 °C. The gas was then fed again to the cooling fans of the clinker cooler. At the same time the material inside the cooler was transported by the moving grate all the way through the cooler and got finally discharged at the end of the cooler via a clinker hopper. With the help of a screw conveyor the clinker was then carried to the main cold clinker extraction system or, for chemical analysis of the clinker, to a manual clinker extraction point.

The input parameters from the pilot cooler tests (WP9) to the process modelling (WP6) are:

- Cooling rate / heat recuperation
- Leakage of air to the oxyfuel clinker cooler
- Clinker quality of the clinker cooled with oxyfuel technology

Cooling rate / heat recuperation

With the help of cooling curves received from the experimental testing the cooling rate of the two different operational modes (oxyfuel -mode and air-mode) can be compared. The modelled clinker cooler could be validated on the basis of comparing simulated and calculated cooling curves, which are based on the experimental data.

The calculation of the cooling curves from the prototype testing was based on rather imprecise experimental data, for which reason the calculated curves of WP 9 show significant uncertainties

(Figure 4-13). These results relate to WP9 report D9.2. Due to lack of better information, previous cooling curves, which are based on industrial best practice, were considered as corresponding to the prototype test results and valid.

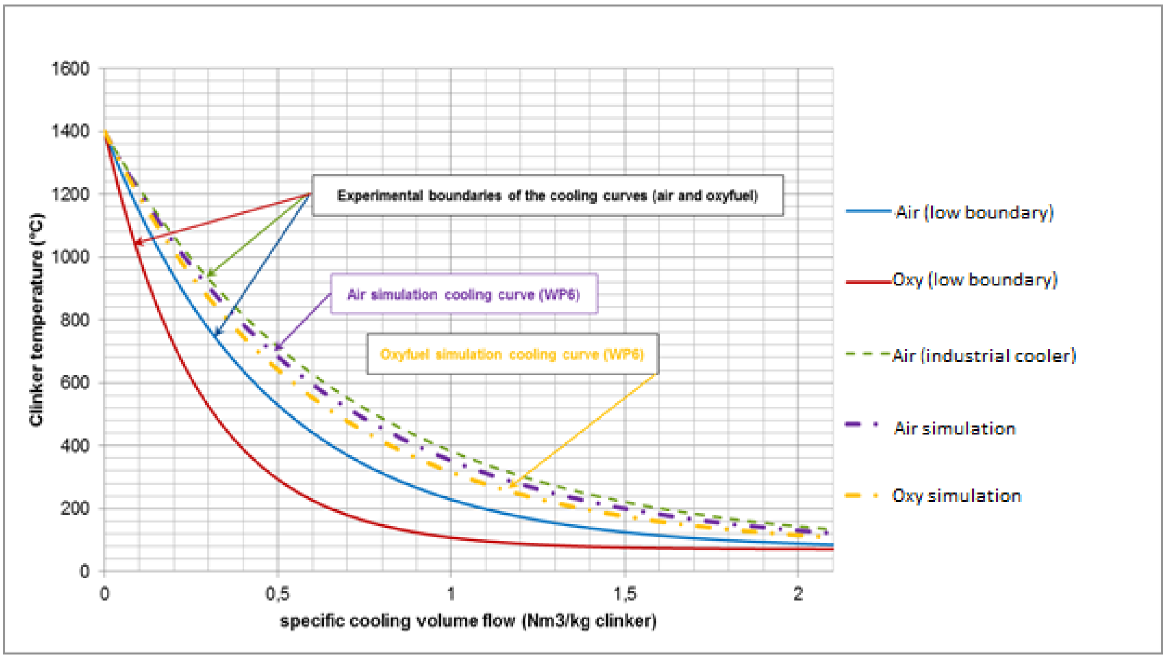

Figure 4-13: Experimental boundaries of the cooling curves with air and oxyfuel cooling medium (D9.2)

Leakage of air to the oxyfuel clinker cooler

From the industrial prototype testing it could be concluded that most of the false air ingress in an industrial scale oxyfuel clinker cooler enters the system through the clinker crusher.

In WP9 the false air ingress to an industrial scale oxyfuel clinker cooler has been roughly estimated using the Bernoulli equation (Table 4-4). False air ingress of about 1,000 Nm^3/h was estimated for a 3000 t/d clinker production.

Table 4-4: False air volume flow through an industrial clinker crusher (3000 t/d)

Number of rollers	Length of rollers (m)	Gap between rollers (m)	Total gap area (m^2)	% total gap area covered with clinker	Pressure difference in clinker crusher (mbar)	False air volume flow (m^3_{stp}/h)
4	5	0.02	0.5	90%	0.2	~ 1000

Clinker quality under oxyfuel conditions

The analysis of clinker by microscopy in WP9 indicated that high CO_2 concentration in the cooling medium alone has no impact on the clinker quality. But in presence of water and CO_2 in the cooling medium unusual layers of up to 2 µm thickness around alite crystals in contact with pores have been observed. The observations indicate that they probably consisted of very fine grained belite and free lime crystals, resulting from alite decomposition. This observation leads to new research questions [LIN-17]:

(1) How does the detected layer affect cement properties?
(2) How are alite decomposition and layer formation related to the presence of water in conjunction with CO_2 in the cooling medium?

In order to answer those two critical and new research questions, VDZ elaborated two more lab experiments, which are currently being carried out. For detailed information see deliverable D9.2 "Analysis of oxyfuel clinker cooler operational performance".

The ECRA CCS project as well as the CEMCAP framework already envisages the construction of a condenser to extract moisture from the recirculated kiln gases originating from raw materials and fuel combustion. The measurement of high moisture content performed in the WP9 cooler prototype testing (Table 4-5) backup the need of a condenser in future industrial scale oxyfuel cement plants.

Table 4-5: Cooling medium moisture content

Cooling medium	CO_2 (vol.% - dry)	Moisture (vol.%)
Air	0.0	8.0
CO_2-rich gas	74.0	13.0

The process model already includes the condenser and therefore the dependence between the cooling medium moisture content and the clinker quality is not considered. As the above mentioned impact on the clinker quality could not be observed at dry flue gas recirculation, the model assumptions are still valid.

5 HEAT INTEGRATION PROCEDURE

The primary heat source is the exhaust gas leaving the preheater and the primary heat sink is the heat required for drying of the raw material in the raw mill. Additionally, the compression heat from the ASU air compression and CO_2 compression train can also be treated as potential heat sources in the process. Based on the quality of excess heat available (temperature level) after satisfying the requirements of the heat sink (raw material drying), a suitable Organic Rankine Cycle (ORC) can be designed.

Thus, the focus of the heat integration work is to develop a network that maximizes power output from the rankine cycle.

5.1 Heat integration model

The Sequential Framework for heat exchanger network synthesis [ANR-11], which is a user driven automated procedure developed at Norwegian University of Science and Technology NTNU for the design of heat exchanger networks, has been used to perform heat integration. The sequential and iterative method, shown in Figure 5-1, has been developed as a compromise between Pinch Design Method [LIB-83] where all trade-offs are usually not accounted for, and computationally intensive Mixed Integer Non-Linear Programming (MINLP) models where all trade-offs are handled.

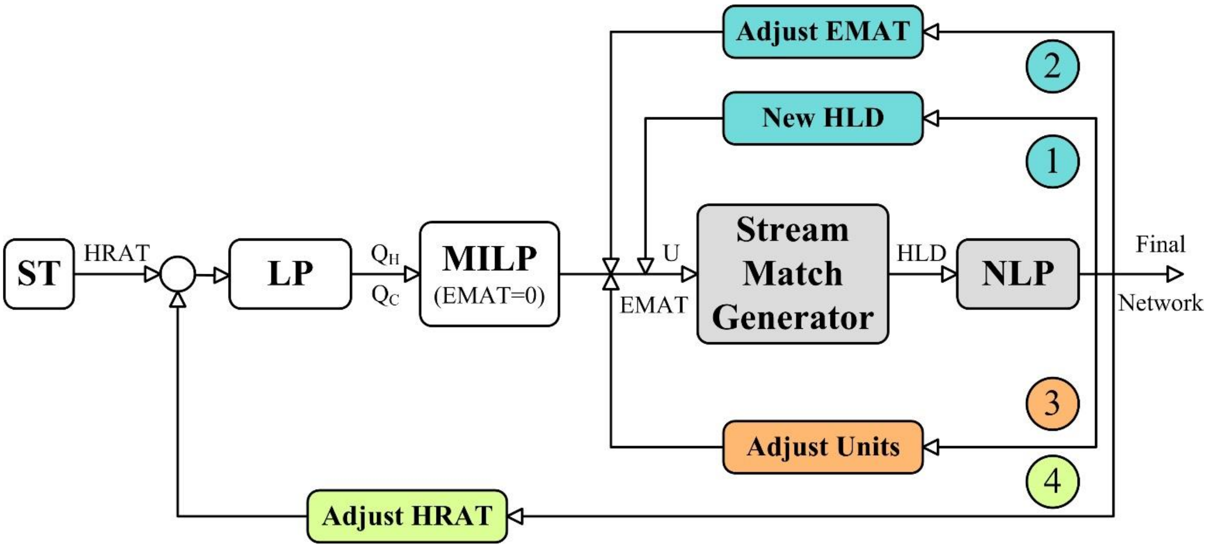

Figure 5-1: The Sequential Framework for Heat Exchanger Network Synthesis

The subtasks of the process are solved sequentially using Mathematical Programming. Briefly, these steps involve:

- Establishing the minimum energy consumption (LP),
- Determining the minimum number of units (MILP),
- Finding sets of matches and corresponding heat load distributions (HLDs) for minimum or a given number of units (MILP), and
- Network generation and optimisation (NLP) as shown in Figure 5-1.

SeqHENS has been developed as a semi-automatic design tool for synthesis of heat exchanger network using the Sequential Framework. This allows for significant user interaction in the synthesis process. More details regarding the optimisation procedure and models can be found in [ANR11].

To better understand the results produced by SeqHENS and the optimisation procedure, visual tools of Pinch Analysis [LTB-82] are used in this report to provide insight into heat integration. The visual tools of Pinch Analysis used are the Composite Curves and the Grand Composite Curves and are briefly explained below for convenience.

The Composite Curves (CC) of Pinch Analysis are temperature versus enthalpy curves that are used to identify targets for heat exchange: One for hot streams that require cooling and the other for cold streams that require heating. Figure 5-2 shows an example of Composite Curves.

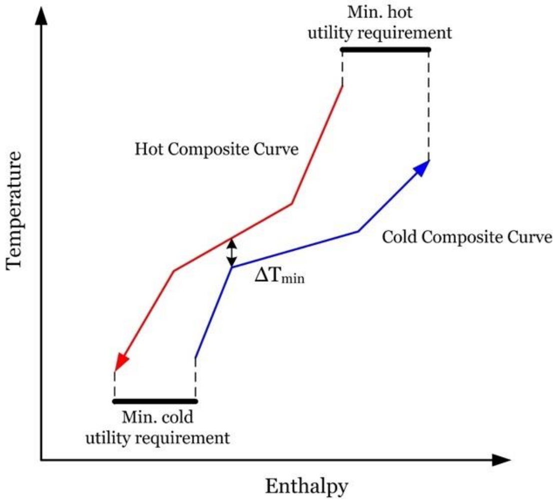

Figure 5-2: Composite Curves

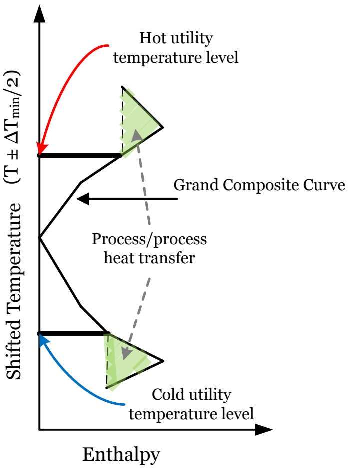

Figure 5-3: Grand Composite Curve

In addition to the composite curves, Grand Composite Curves (GCC) play an important role in Pinch Analysis. GCC is a shifted temperature[1] versus enthalpy curve as shown in Figure 5-3, that enables identifying utility levels to achieve the minimum hot and cold utility requirements set from the Composite Curves.

The composite curves and grand composite curves are presented where required to provide insight into the results obtained with details on how they are used.

5.2 Organic Rankine Cycles

Given the low temperature waste heat available in a cement oxyfuel plant (around 390 °C), there isn’t sufficient temperature level for superheating when applying a steam rankine cycle. Superheating is required to prevent condensation in the steam turbine as the working fluid, water, is a wet fluid. Thus, Organic Rankine Cycles (ORC), which are based on dry organic fluids, that do not require any superheating are ideal for use in these conditions.

A basic ORC consists of four processes: increasing pressure of the working fluid through a pump, high temperature heat addition through an evaporator, expansion of the high temperature

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[1] Shifted temperature is (stream temperature – $\Delta T_{min}/2$) for hot streams and (stream temperature + $\Delta T_{min}/2$) for cold streams such that at the pinch point, where the difference between hot and cold temperatures is ΔT_{min}, the hot and cold streams meet,

as well as high pressure fluid through a turbine, and low temperature heat rejection through a condenser. The schematic of a basic ORC is shown in Figure 5-4. In case of dry fluids, the state point after the expansion in the turbine lies in the superheated vapor region. As the temperature of the superheated vapor at the turbine outlet is more than that of the liquid at the inlet of the evaporator, it is possible to improve thermal efficiency of the cycle through a regenerator[2].

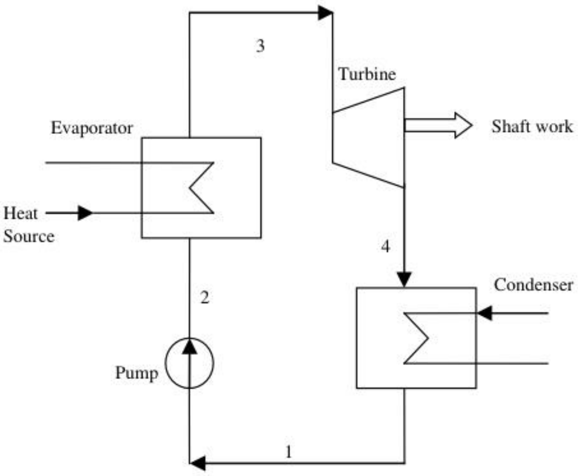

Figure 5-4: Schematic diagram of a basic ORC

Three different working fluids, shown in Table 5-1 below, are chosen as prospective candidates based on the temperature level.

Table 5-1: Properties of selected ORC working fluids

Working fluid	$P_{critical}$ (bar)	$T_{critical}$ (°C)
n-hexane	30.3	234.7
n-pentane	33.7	196.6
n-butane	38.0	152.0

5.3 Other considerations

Due to the reduction of heat transfer by dust layers on the transfer areas, the utilization of the preheater exhaust gas for direct heat integration is difficult. In this case comprehensive cleaning efforts become necessary, for which reason an intermediate hot oil circuit is used to transfer heat from the exhaust gas to the different heat sinks. For the purposes of this work Dowtherm G was chosen as the heat transfer fluid used in the hot oil circuit. Dowtherm G can be used up to a temperature of 380 °C. The thermal and physical properties of the Dowtherm G fluid used in this work are available at Dow website[3]. The minimum pinch point temperature difference between the exhaust gas and hot oil is set to 80°C and that between the hot oil and other streams is set to 20 °C based on recommendations from D3.2 CEMCAP framework for comparative techno-economic analysis of CO_2 capture from cement plants.

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[2] where the evaporator inlet is preheated by the turbine outlet

[3] https://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0032/0901b803800325da.pdf?filepath=/heattrans/pdfs/noreg/176-01353.pdf&fromPage=GetDoc

6 OXYFUEL OPTIMAL OPERATIONAL SETTINGS

6.1 Adaptation of the process parameters

In order to improve the accuracy of the oxyfuel clinker burning process the following equipment parameters were adapted to the experimental results during the CEMCAP project

- Burner specifications
    - Primary and secondary air compositions and volume flows
- Calcination process
    - Calcination start- and end temperature
- Cooler
    - False air ingress

The experimental results have confirmed that the following assumed parameters, which were determined in the ECRA CCS project [ECR-12] are valid assumptions for the simulation of the clinker burning process under oxyfuel conditions.

- Calcination process
    - Residence time of 3 s
- Cooler
    - Cooler efficiency / heat exchange between the cooling medium and the clinker under oxyfuel conditions
    - Clinker quality under oxyfuel conditions

After the individual adaptation of the equipment units to the experimental findings in the VDZ process model all adapted operation units were combined. In order to optimise the energy efficiency of the clinker burning process a parameter study for the refined oxyfuel clinker burning process was carried out. In the following the kiln unit settings, which were determined for the optimised clinker burning process are described.

6.2 Optimised equipment settings

The clinker production process consists of a 5-stage single string preheater tower, calciner with tertiary air duct, rotary kiln and grate clinker cooler (oxyfuel design). The plant's geometry, raw material composition and used fuels conform to the data described in CEMCAP's framework document D3.2. The simulation based on the refined model results in a clinker production of 125,112 kg/h (3,003 t/d). A flue gas recirculation rate of 0.55 has been established.

Cooler settings

In order to ensure a proper cooling of the hot clinker to cold clinker temperatures of 86 °C a cooling medium is supplied to the cooler with a rate of 1.74 m^3_{stp}/h. Table 6-1 lists the detailed distribution of gas streams.

Table 6-1 Cooler gas flow specifications

	Volume flow in m^3_{stp}/h	Spec.volume flow in $m^3_{stp}/kg_{clinker}$	Temperature in °C
Cooling medium	222,680	1.78	24
Secondary gas	28,547	0.22	984
Tertiary gas	77,759	0.62	907
Recirculated flue gas	116,172	0.92	338

The available waste heat from recirculated flue gas (including dust) amounts to 11433 kJ/s. This heat is extracted by a heat exchanger and could additionally be used for drying purposes. The clinker cooler performs very well with an energy efficiency of 86%.

Preheater settings

In order to ensure the function of the preheater cyclone a certain volume flow is needed at given geometry resulting in gas velocities of 15 to 20 m/s. (requirement with regard to retrofit). Table 6-2 lists the cyclone specification and gas temperature profiles along the preheater tower.

Table 6-2 Cyclone specification

Cyclone Number	Size, entrance area	Gas velocity	Gas exit temperature
2 (bottom cyclone)	11.85 m^2	14.9 m/s	790 °C
3 (mid cyclone)	10.95 m^2	15.4 m/s	714 °C
4 (mid cyclone)	9.80 m^2	16.1 m/s	589 °C
5 (top cyclone)	8.25 m^2	16.8 m/s	394 °C

The flue gas leaving the plant shows relatively high temperature when 5 cyclone stages are installed. This is due to the calcination at higher temperatures, but especially to the changed gas properties resulting in energy shifting compared to air fired plants. The CO_2 concentration on dry basis amounts to 83.4 vol.% (Table 6-3), which is an excellent high level with regard to the required final purification of CO_2.

Table 6-3 Flue gas specification

Components and gas conditions	Value
Ar	1.19 vol.%
Cl	0.00055 vol.%
CO_2	76.97 vol.%
H_2O	7.74 vol.%
O_2	3.35 vol.%
N_2	10.75 vol.%
SO_2	0.0083 vol.%
Temperature	394°C
Volume flow, stp dry	150,212 m^3_{stp}/h
Spec. volume flow	1.2 $m^3_{stp}/kg_{clinker}$

About 34,556 kJ/s (994 $kJ/kg_{clinker}$) of waste heat is available from the flue gas including dust. This energy will be either used for the raw material drying or to generate electricity in the ORC unit.

This project has received funding from the European Union's Horizon2020 Research and Innovation Programme under Grant Agreement No 641185

Calciner settings

About 58% of the fuel is supplied to the calciner. In order to ensure a proper combustion the oxygen concentration of the carrier gas at the calciner was increased (see below for reasons). For the reason of equipment protection and to avoid unwanted coating in the calciner, the temperature in the calciner is only slightly higher than the usual temperature levels. Due to the shift of reaction equilibrium to higher temperatures the degree of calcination is lower than in the reference air case. Thus remaining calcination reaction has to take place in the kiln inlet zone.
At the bottom end of the calciner a degree of calcination of 82% could be established. This is still on a very good level and limits the share of calcination required to be performed in the kiln inlet to 18%.

Table 6-4 Calciner specifications

Description	Value
Fuel input (coal)	8,350 kg/h
Primary gas (including additional oxidizer)	2,030 m^3_{stp}/h
Outlet temperature	905°C
Degree of calcination, calciner outlet	82%

Rotary kiln settings

Flame formation and consequently heat transfer are strongly influenced by the oxyfuel operation, more precisely by the changed kiln atmosphere. In order to maintain a high clinker quality the compliance with specific temperature profiles in the kiln is extremely important.

Based on the model adaptations of the burner configuration described above (see section 4.3), the following process parameters have been set.

- The oxygen concentration in the primary gas was increased from 35 vol.% to 52 vol.%
- The oxygen concentration and the volume flow of the secondary gas was decreased (from 22 vol.% to 21 vol.% and from 36,787 m^3_{stp}/h to 28126 m^3_{stp}/h) due to the high oxygen concentration in the primary air.
- The oxygen concentration of the carrier gas at the calciner was increased from 21.4 vol.% to 24.5 vol.% in order to compensate the missing oxygen resulting from the oxygen reduction in the recuperation gas.

These settings led to the operational parameters listed in Table 6-5 and the temperature profiles. The oxygen concentration is on a low level, but still ensures oxidizing atmospheres to avoid colour changes of the later cement. Kiln inlet temperatures should be below 1,200 °C to avoid formation of excessive incrustations.

Table 6-5 Kiln main operational parameters

Description	Value
Fuel input (coal)	6,120 kg/h
Sintering zone temperatures	1,455 °C
Temperature at kiln inlet	1,147 °C
O_2 level at kiln inlet	0.8 vol.%
Dust content at kiln inlet	318 g/m^3_{stp}

6.3 Optimised PM simulation results

The following Figure 6-1illustrates the kiln heat radiation profiles (on the left kiln inlet and right kiln outlet/burner) for three different operational conditions. The blue curve represents the simulated clinker burning process of the air reference case (BAT3000), the red curve illustrates the simulated oxyfuel operation based on the previous theoretical assumptions [ECR-12] and the green curve the simulation results of the oxyfuel operation after the optimisation of the VDZ process model.

Because of the CO_2 rich atmosphere and a strong activity of Boudouard reaction ($C + CO_2 \rightarrow 2 CO$) the local carbon monoxide concentration in the near burner region is relatively high for the oxyfuel case [ECR-12]. This effect has an impact of the flame characteristics. The flame gets longer with lower peak temperature. Due to the combustion of CO produced by the Boudouard reaction and different heat transfer coefficients of CO_2, energy is shifted from the sintering zone further into the kiln inlet (Figure 6-1). By adapting the burner setting as described above the heat radiation profile in the refined oxyfuel model could be matched to the reference air case, especially at its maximum, leading to the required same heat transfer from the gas to the material. It can be expected that the coating behaviour of the material in the kiln and the thermal load of the rotary kiln is similar for these both cases and therefore fulfil the optimum operational mode.

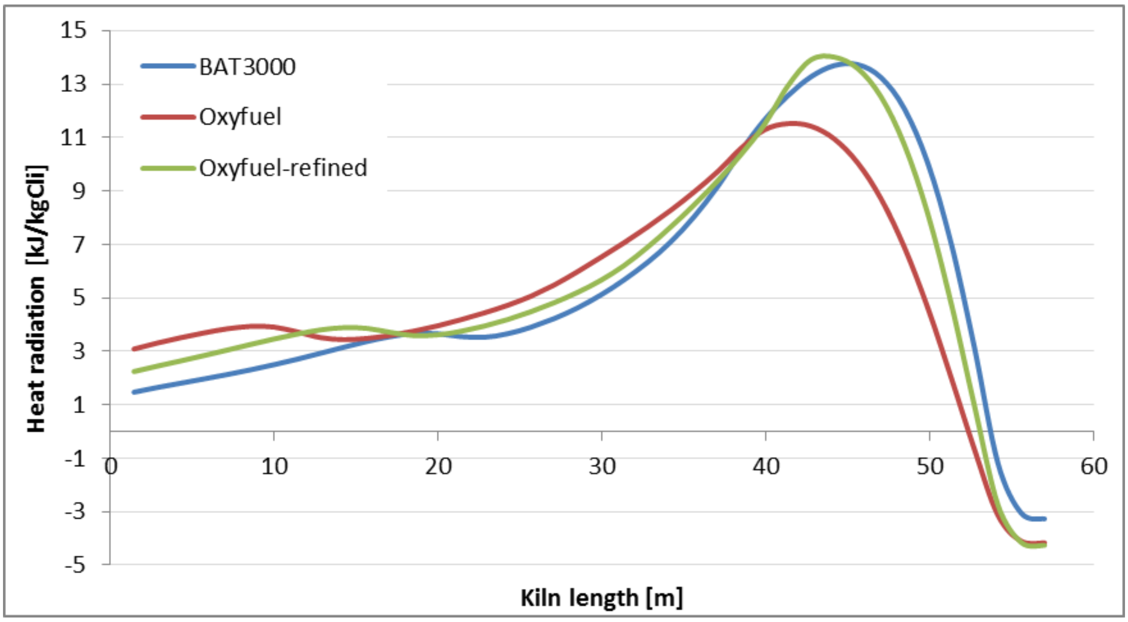

Figure 6-1: Heat radiation profile for three different simulation cases

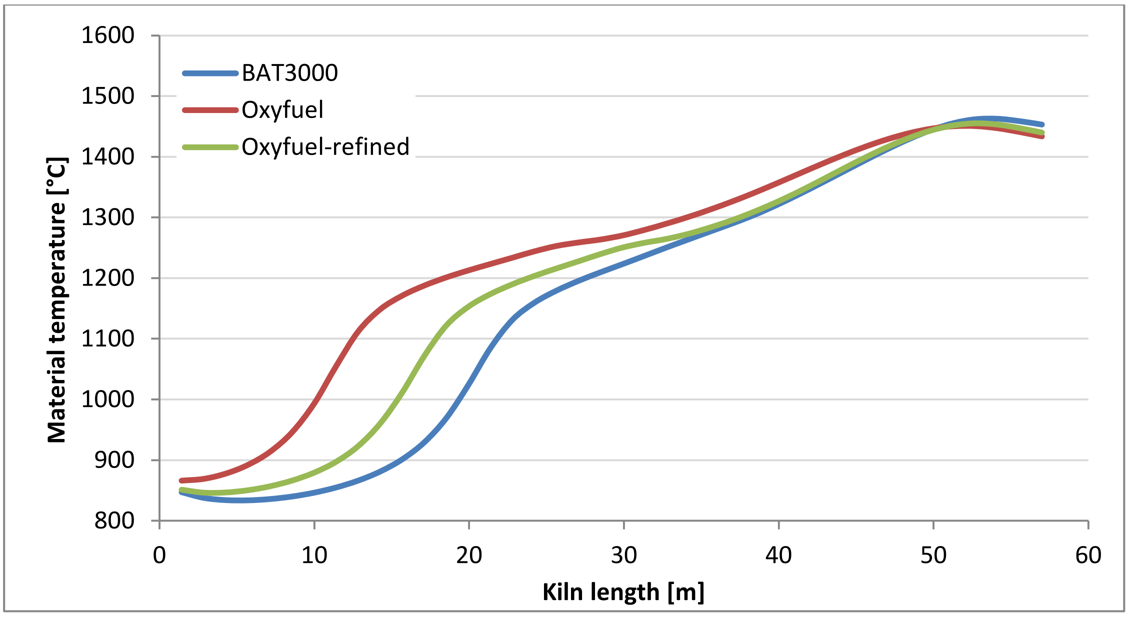

Figure 6-2: Material temperature profile for three different simulation cases

Figure 6-2 shows that the material temperature profiles of the refined oxyfuel operation and the simulated material temperature profile of the air case (reference case) are quite similar. The previous oxyfuel model setting (red line [ECR-12]) differs more significantly from the optimum air case. By adapting the burner the heat transferred to the material in the sintering zone is adequate. The difference of material temperature in the kiln inlet originates (i) from the different gas properties resulting from the gas compositions (influencing the convective heat transfer) and (ii) from the calcination reaction, which is partly shifted to the kiln inlet. The effect can be observed in the formation of the clinker minerals along the kiln (Figure 6-3). Due to the slightly higher material temperatures in the kiln inlet and transition zone in oxyfuel operation the formation of the clinker phases starts earlier in the kiln.

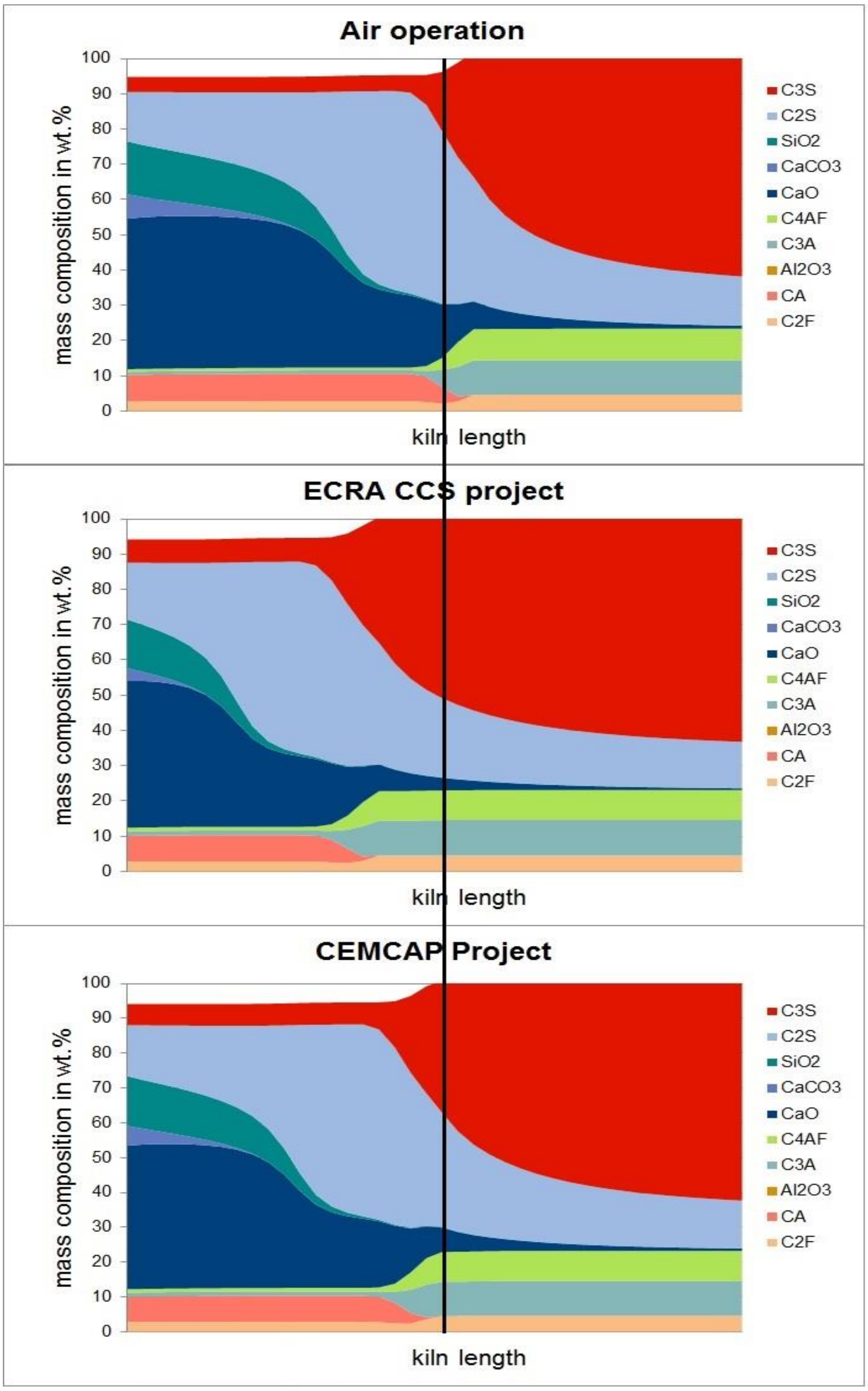

Figure 6-3: Clinker minerals formation along the kiln for three different operation conditions

After the PM adaptation and optimisation the clinker phase formation could be optimised.

Clinker quality

The clinker composition simulated in the optimised oxyfuel operation (CEMCAP project) is similar to the simulation results based on theoretical assumptions (ECRA CCS project) (Table 6-6).

Table 6-6: Clinker compositions for the three different simulations cases

Description of clinker minerals	Air case (BAT3000)	Oxyfuel (ECRA CCS)	Refined oxyfuel (CEMCAP)
C_3S [%]	64.48	65.46	64.73
C_2S [%]	13.82	13.07	13.63
C_3A [%]	9.82	10.08	9.98
C_4AF [%]	8.92	8.47	8.69
C_2F [%]	0.36	0.60	0.48
CAO [%]	0.78	0.44	0.60

But for the hydraulic properties of the clinker not only the mineralogical composition of the clinker is important. The crystal structure of the clinker has a significant impact on the clinker properties. For a satisfying crystal structure of clinker rapid rate of heating, a sufficiently long time at high temperature, an adequately high maximum temperature and a rapid cooling in the kiln are required [DOH-13].

Although the crystal structure of the clinker cannot be simulated with the VDZ process model, the amount of formed clinker phases based on thermodynamic equilibrium gives information about the expected high quality of the clinker in the optimised PM simulation results. Moreover, with the help of the material temperature profile the clinker burning conditions regarding the crystal structure of the clinker could be evaluated.

Energy balance of the clinker burning process

The fuel energy demand of the clinker production process amounts to 3,140 $kJ/kg_{clinker}$ which is + 3.8% compared to air reference case. Table 6-7 illustrates the distribution of the energy streams.

The comparison of the energy balances shows clearly the energy shift in the clinker production process when applying oxyfuel technology. E.g. as shown above the energy is shifted from the sintering zone to the kiln inlet due to the differing gas properties. For that reason more energy is needed in the kiln and less in the calciner firing (oxyfuel: 42%/58% and air case: 38%/62%). Moreover more energy is leaving the plant by flue gas enthalpy due to higher heat capacity of the CO_2 compared to N_2. On the other hand waste energy from cooler exhaust is reduced, as CO_2 rich gas can recuperate more energy from the hot clinker in the cooler. However, the sum of both streams shows that the available waste heat is about 17% higher than in the air case causing the increase in total energy demand.

Table 6-7 Energy balance of the clinker production process

Description	Oxyfuel case in kJ/s	Oxyfuel case in kJ/kg$_{clinker}$	Air case in kJ/kg$_{clinker}$
Input			
Raw material	3,003	86.4	86.5
Cooling gas	1,726	71.5	36.4
False air	46	1.5	1.3
Fuel, kiln	46,155	1,327.9	1,149.0
Primary gas, kiln	35	1.0	1.4
Fuel, calciner	62,973	1,811.8	1,876.6
Primary gas, calciner	13	0.4	0.3
Sum of input	113,951	3,299.5	3,151.5
Output			
Flue gas incl. dust	34,556	994.2	659.9
Cold clinker	2,095	66.4	87.7
Cooler exhaust gas (Air), recirculated gas (Oxy) incl. dust	7,923	329.0	402.0
Wall losses	10,467	301.1	305.9
Reaction enthalpy of the material	58,910	1,608.8	1,696
Sum of output	113,951	3,299.5	3,151.5

6.4 Waste heat recovery and heat integration for the optimised oxyfuel clinker burning process

Available waste heat source from the cement clinker burning process are cooler exhaust and preheater exhaust gas. Although heat from wall losses sum up to around 10% of the energy input, still no adequate technology exits to recover those. Usually the waste energy especially from flue gas is used for drying the raw material. To avoid massive air in-leaks in the mill and resulting dilution of the flue gas a comprehensive heat recovery system is used for the oxyfuel technology as shown in Figure 2-1. An additional source of low grade heat is from the intercoolers in the CO_2 compression process of the CPU.

The first step in the heat integration process is using the hot oil to extract heat from the preheater flue gas. The composite curves of this step are shown in Figure 6-4 below. Notice that the curves are wide apart indicative of the high minimum temperature difference of 80 °C. The exhaust gas is available at 394 °C, however due to the 80 °C temperature different, the hot oil is heated up to 314 °C.

This hot oil is now available as a heat source is the next step for heat integration along with CO_2 compression intercoolers. The heat available from these sources is shown in Figure 6-5. There are 3 heat sinks:

- Preheats air for drying the raw meal. Here 15 °C ambient air is heated to 202.9 °C. The duty is 6352 kW.

- The high pressure N_2 rich vent gas from the CPU is preheated to 200.4 °C from 20.4 °C prior to the expander. The duty is 1182 kW.
- The outlet of the expander is then heated from 10 °C to 70 °C before it is sent to the stack.

These heat sinks must be first integrated into the process to identify heat available for the ORC process. The GCC is shown in Figure 6-6 where these heat sinks have been incorporated. This GCC can be used to target for the ORC cycle design.

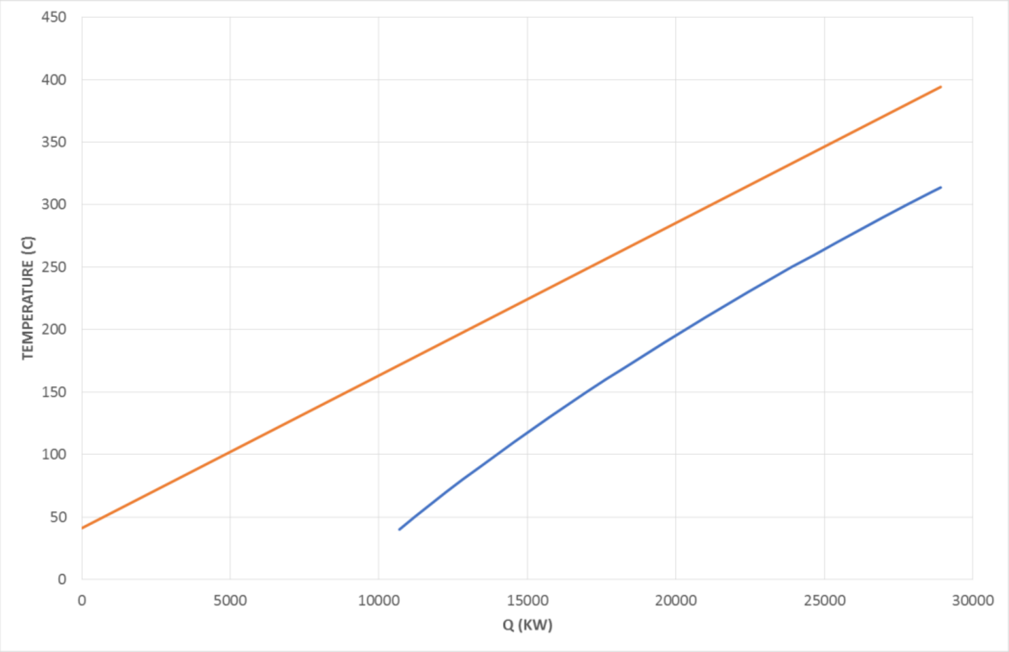

Figure 6-4: Composite curves for the preheater exhaust - hot oil heat exchange

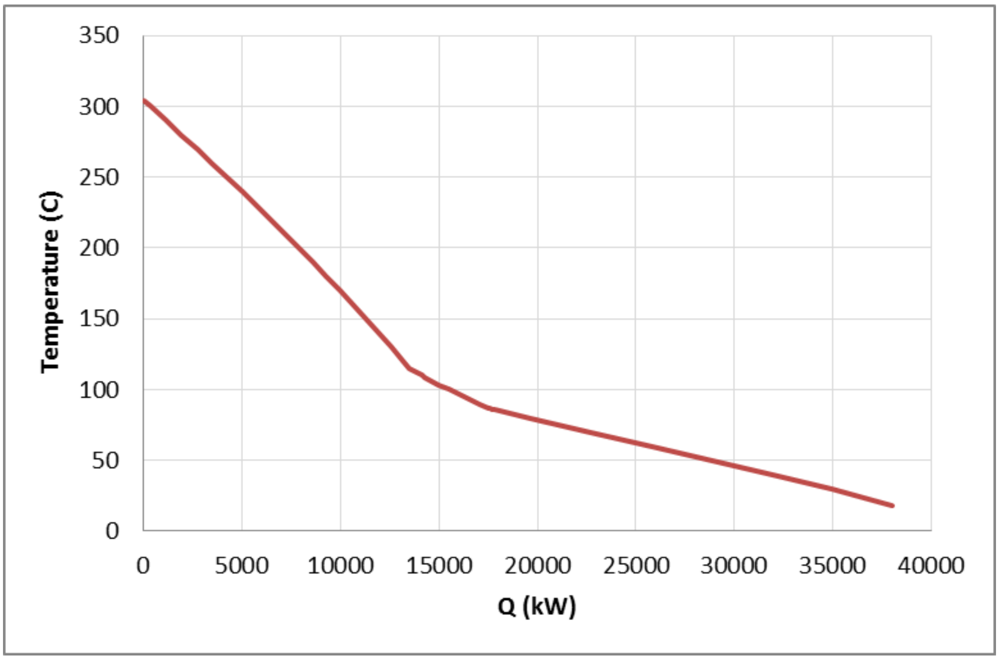

Figure 6-5: Grand Composite Curve showing heat available from the different heat sources

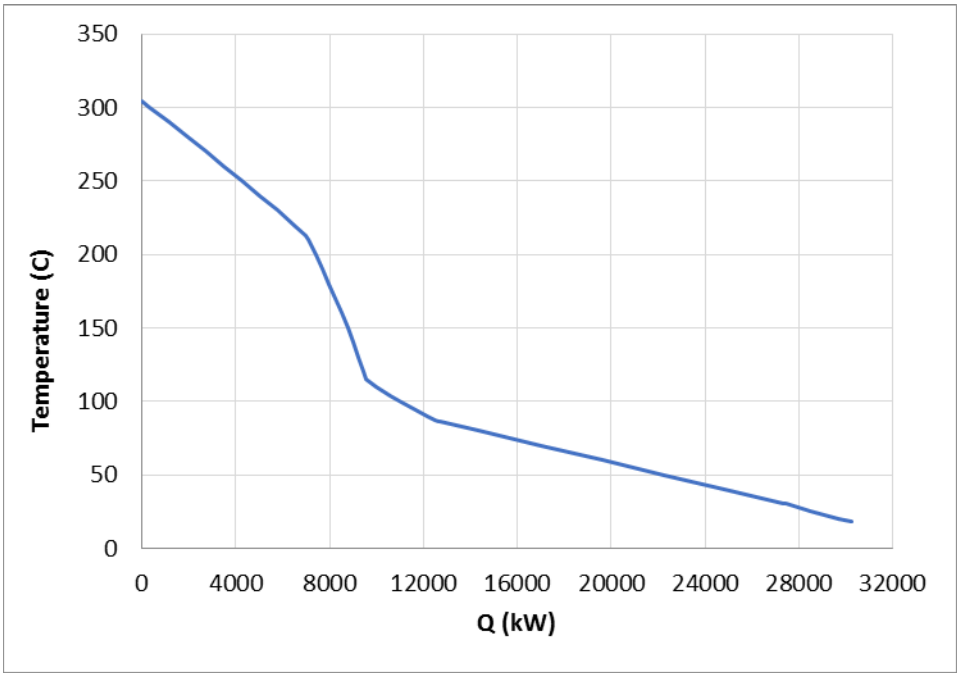

Figure 6-6: GCC of the process including the three heat sinks

Notice that the heat available has reduced (x-axis) and that there is a change in the shape of the curve above 114 °C. This is due the integration of heat sinks. The ORC can be targeted based on this GCC.

The GCC with the evaporator (horizontal line) and economizer of the 3 different ORCs are shown in Figure 6-7. Note that the values shown in this curve are approximate and for didactic purposes only. From the figure it is clear than the ORC with n-Butane as the working fluid is able to utilize the most heat available in the streams. This is borne out by the work produced by these three processes. The power output of the three ORCs are: 1.975 MW with n-Hexane as working fluid, 2.510 with n-Pentane as working fluid and 2.900 with n-Butane as working fluid.

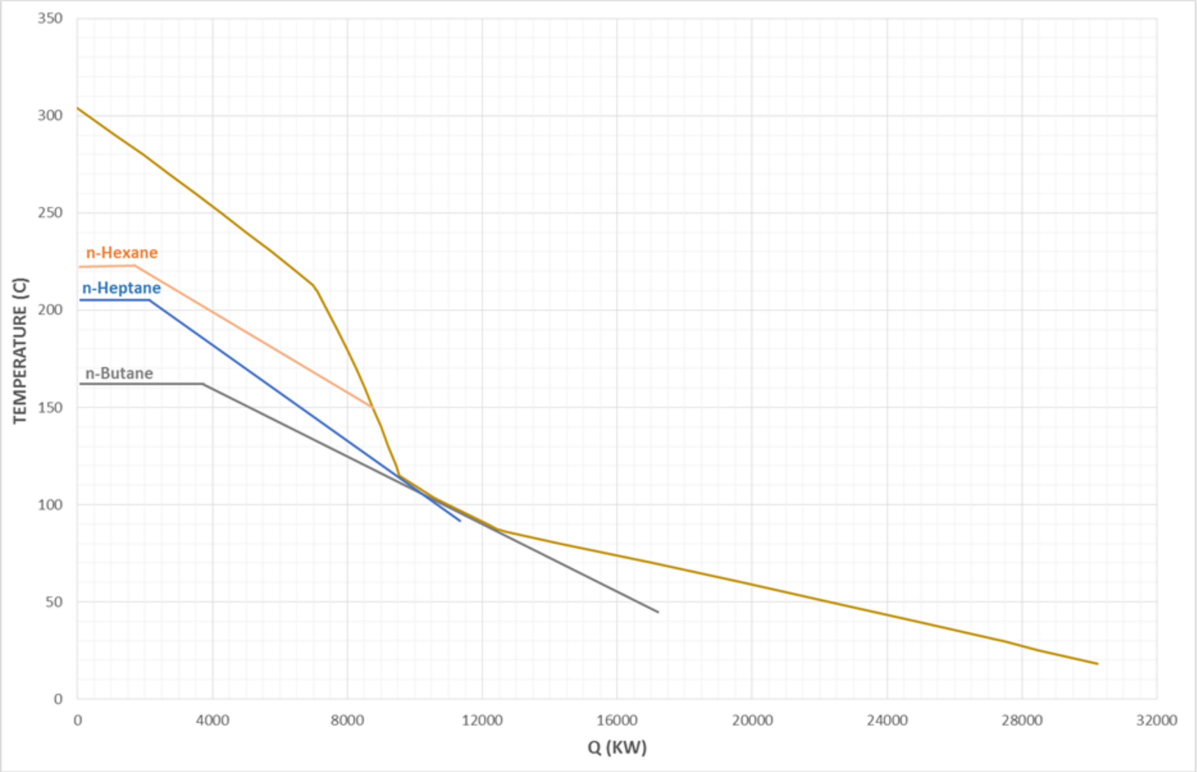

Figure 6-7: GCC with the 3 ORCs targeted

The composite curve of the process with n-Hexane as working fluid is shown in Figure 6-8. The ORC with n-Hexane as working fluid does not utilize heat below 140 °C. This can be seen from the GCC of the process with n-Hexane as working fluid shown in Figure 6-9. Thus is possible to consider a bottoming ORC with an 80-100 °C cycle. A quick evaluation shows that the resulting power output from the two cycles would be around 2.7 MW, still lower than the case with n-Butane as the working fluid while also being more expensive.

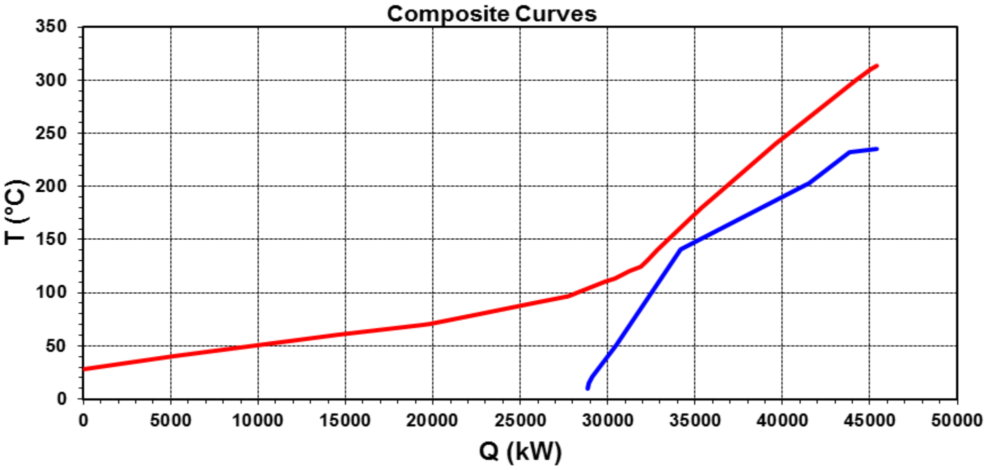

Figure 6-8: Composite curve – nHexane

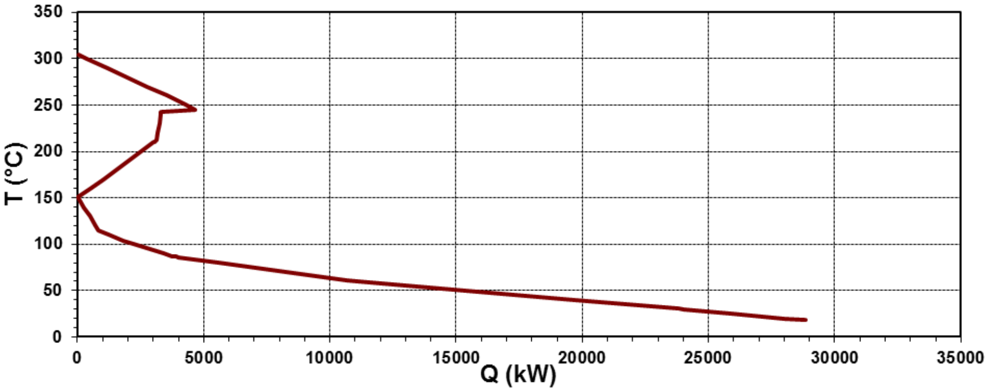

Figure 6-9: GCC – nHexane

The composite curves and grand composite curves of the process with n-Pentane and n-Butane as presented in Figure 6-10 to Figure 6-13. Here is can be seen that the heat is better utised and the waste heat after integration with the ORC is available at much lower temperature (below 100 °C for n-Pentane and below 80 °C for n-Butane).

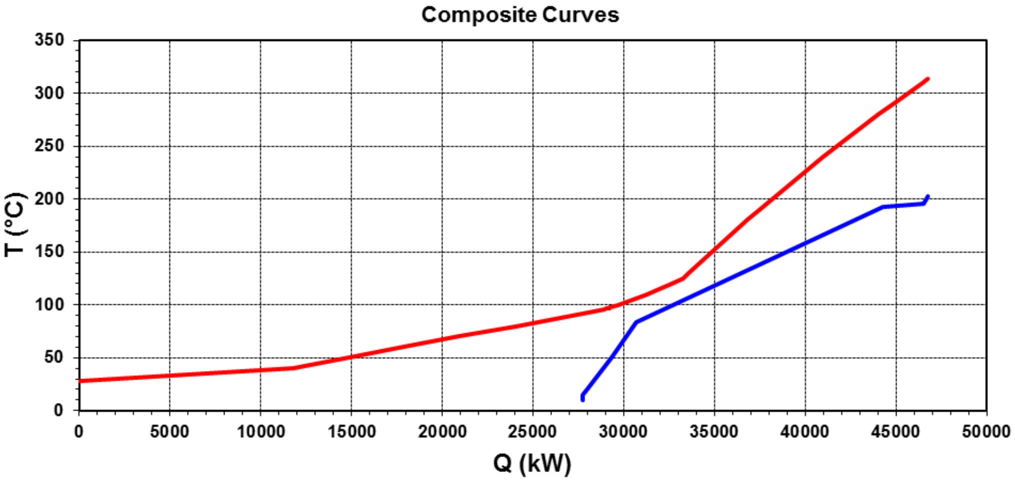

Figure 6-10: Composite curves - nPentane

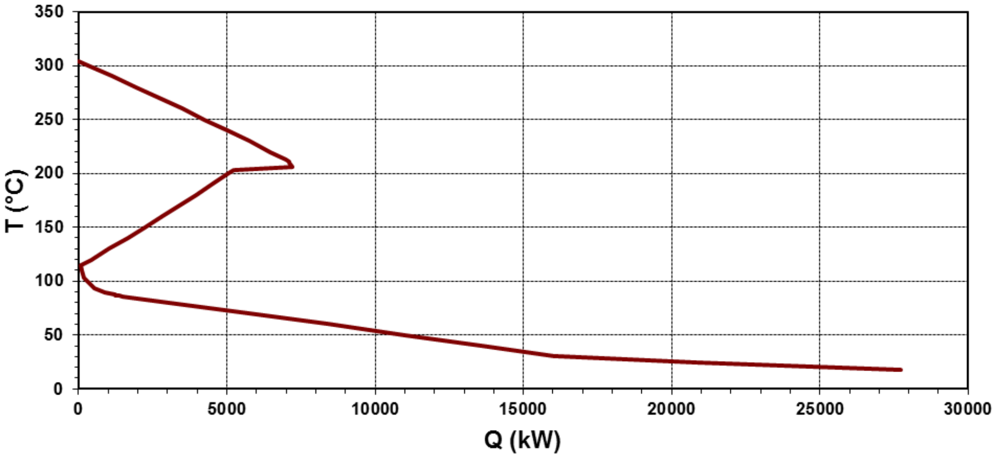

Figure 6-11: GCC – nPentane

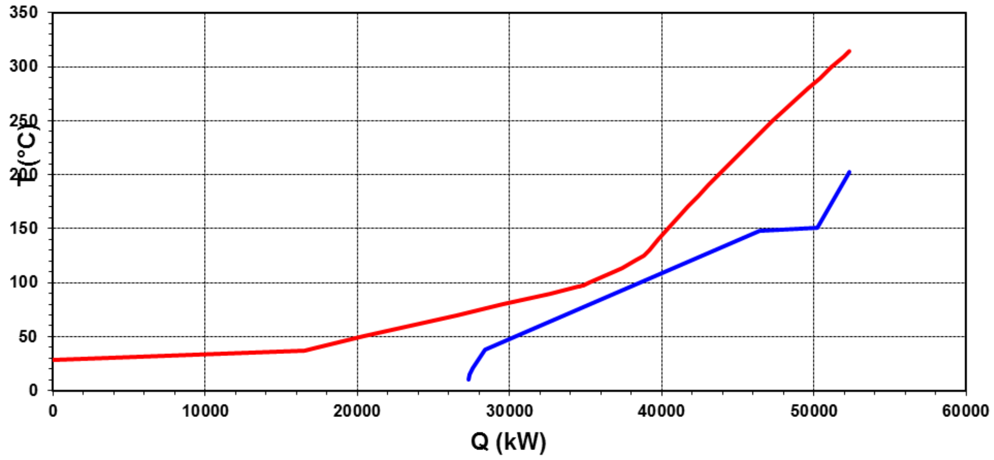

Figure 6-12: Composite curves – nButane

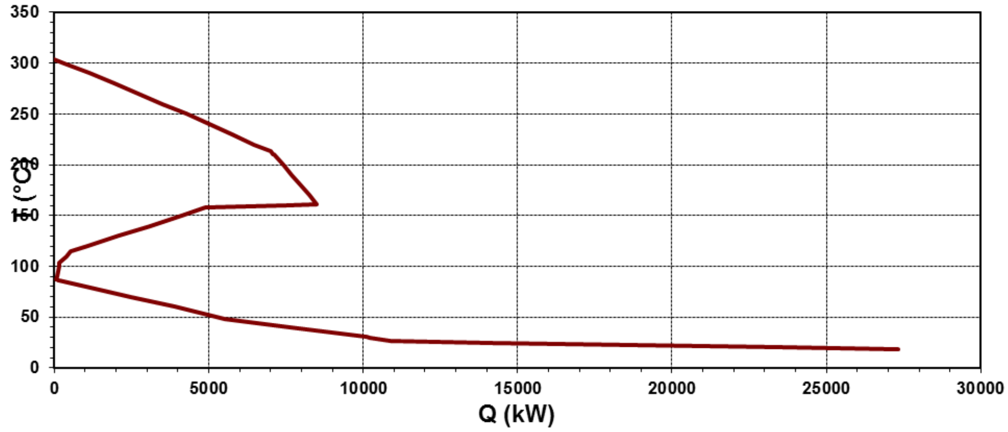

Figure 6-13: GCC - nButane

As mentioned earlier, the minimum temperature difference is set to 20 °C for these cases. If the minimum temperature difference is reduced to 10 °C, the n-Pentane ORC can produce 14.3% more power while the n-Butane ORC can produce 15.2% more power. The minimum temperature difference is an economic parameter as there will be a trade-off between increased power output and increased cost for the equipment due to an increase in heat exchanger area. Optimisation of the minimum temperature difference is out of scope of the present work but should be taken into account for an eventual optimised process design.

Another option to improve heat integration is by improved design of the heat transfer fluid loop. A single loop has been considered. However multiple loops can further optimise heat integration and relax the “kinks” that cause pinch in the process. Again, this should be considered while performing a detailed design of the process.

The operational performance of this case, henceforth called base case, is presented below.

Table 6-8: Operational performance of the base case

Operational performance		
False air	%	6.3
Clinker prod	t/h	125
Fuel Input	MWth	109.0
O_2 flow	t/h	31
ASU power	MWe	7
ASU dehydration	MWe	0.53
Recycle blower	MWe	0.54
CPU power	MWe	11.5
CPU dehydration	MWe	0.6
Sp power consumption	kJ/kg_{CO2}	417.7
ORC	MWe	2.9
Net power	MWe	13.2
Cooling duty	MWth	42.7
Condenser duty	MWth	15.3
CCR	%	90.0
CO_2 purity	%	97.3
CO_2 captured	t/h	98.8
CO_2 emissions	t/h	11.0
CO_2 emissions	$kg_{CO2}/t_{clincker}$	87.8

Influence of preheater stages on heat integration/power generation

Basically, the number of preheater stages is defined by the raw material moisture and the respective energy needed for the drying, as flue gas is usually used for this purpose. Also in oxyfuel operation this usage of energy for drying is still of highest relevance to ensure overall energy efficiency and the function of the dry process kiln line. In the reference case a 5-stage preheater tower has been defined in combination with an average raw material moisture of 6%. Related to a remaining moisture of 1% about 250 to 300 $kJ/kg_{clinker}$ is required for the drying in this case. It has to be taken into account, that only energy of above 100°C can be used. Conventionally about 60 to 70% of the flue gas energy can be defined as usable energy. If the moisture content is higher, more energy is extracted from the process by reducing the number of cyclone stages. That way the clinker burning process itself becomes less efficient due to the less efficient material preheating.

However, after drying the flue gas can exhibit still usable energy for e.g. power generation. In order to increase the availability of heat from flue gases a constructional option is the reduction of preheater cyclone stages assuming constant raw material moisture. The balance of benefit and effort is discussed in the following. In order to determine the optimal operation conditions regarding the overall energy efficiency the preheater stages were varied from 5 to 3 stages. The change of operation conditions due to the variation of preheater stages is shown in Table 6-9.

Table 6-9: Simulation results of preheater stage variation

Preheater stages	CO_2 concentration (Flue gas) [%]	Volume flow (Flue gas) [m^3_{stp}/h]	Temperature (Flue gas) [°C]	Enthalpy flue gas + dust [$kJ/kg_{clinker}$]	Energy demand (Clinker burning process) [$kJ/kg_{clinker}$]
5	77	162,813	394	994	3,140
4	77	166,703	433	1,127	3,253
3	77	169,497	483	1,299	3,411

As shown in Table 6-9 the temperature of the flue gas and the energy demand of the clinker burning process increase with decreased preheater stages. That means there is a trade-off between the preheater stages, the thermal energy demand for the clinker burning process and the temperature of the flue gas, which has an impact of the efficiency of ORC system.

As can be seen from Figure 6-14 and Figure 6-15, the GCCs for the 4 preheater stages (referred to as 4PH) and the 3 preheater stages (referred to as 3PH), the amount of heat available and utilized by the ORC increases compared to the 5 preheater stages case (base case). The power output of the ORC increases to 3.4 MWe and 5.1 MWe for the 4 and 3 preheater stages respectively from 2.9 MWe for the base case with 5 preheater stages. That is for the 4 preheater stages case, there is a 0.5 MWe increase in power output for a 4 MWth increase in fuel input. This gives an ORC efficiency of 12.5%. Similarly, the efficiency of the additional fuel used in the 3 preheater stages case is 24.1%. Also, decreasing the number of stages leads to higher energy consumption in the air separation unit (more fuel requires more oxygen for combustion) and CPU (larger volumetric flow).

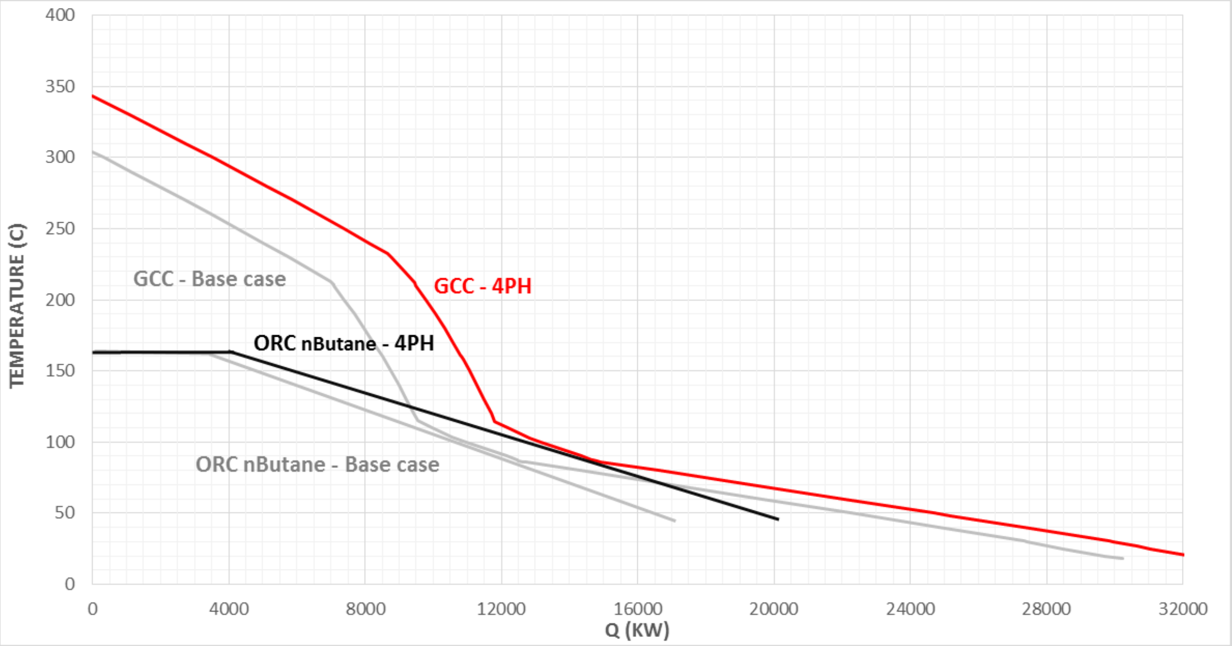

Figure 6-14: GCC – 4 Preheater stages

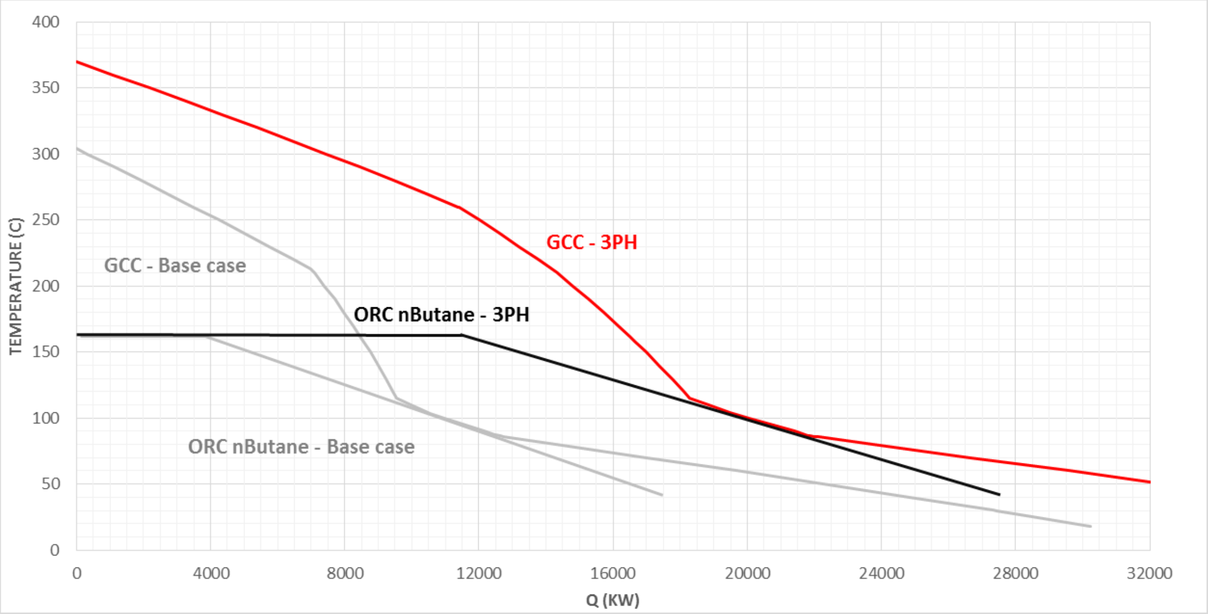

Figure 6-15: GCC – 3 Preheater stages

With the consideration of the increased energy consumptions of ASU and CPU the efficiency of the additional fuel used in the 4 and 3 preheater stages cases are 5.6% and 15.2%.
Table 6-10 lists the input of energy for the clinker burning process and additional oxyfuel units (excluding the base electrical energy demand for gears, mills etc.) for the three different cases.

Table 6-10 Energy in-/output of the scenarios

	Base case, 5 stages	PH 4 stages	PH 3 stages
Energy input (with regard to additional oxyfuel units)			
Clinker burning	109 MW_{th}	113 MW_{th}	118 MW_{th}
ASU (incl. dehydration)	7.53 MW_e	7.53 MW_e	7.73 MW_e
CPU (incl. dehydration)	12.1 MW_e	12.3 MW_e	12.7MW_e
Auxiliaries (blower, condenser)	15.8 MW	17.5 MW	14.9 MW
Delta to base case		6 MW	8.9 MW
Energy generated (output)			
ORC	2.9 MW_e	3.4 MW_e	5.1 MW_e
Delta to base case		0.5 MW	2.2 MW
Total delta to base case		- 5.5 MW	- 6.7 MW

The low efficiencies indicate that decreasing the number of pre-heater stages and increasing the fuel flow and heat available in the system is regarding reduction of CO_2 emission not an interesting option. Moreover the efficiency of a pulverized coal fired power plant is around 40-45% and the efficiency of a typical ORC is around 20-25%. Assuming both systems to use coal as fuel, the onsite power production at less preheater stages generates higher global CO_2 emissions. In summary the production of power makes sense, if waste heat is available anyway but not if the clinker burning process efficiency is decreased.

But from a cost point of view the power generation with the help of the ORC system in the oxyfuel clinker burning process is profitable with following costing information

Table 6-11 Energy prices

	Cost	Unit
Electricity	75	€/MWh
Coal	3	€/GJ

Due to the high electricity costs compared to the coal prices or even prices for alternative fuels, the above described measure becomes profitable at electricity cost levels of 75 €/MWh.

The purchase price of electricity is in several countries higher than this value (*Figure 6-16*) and thus the power generation with ORC in the oxyfuel clinker burning process with increased fuel flow could be interesting.

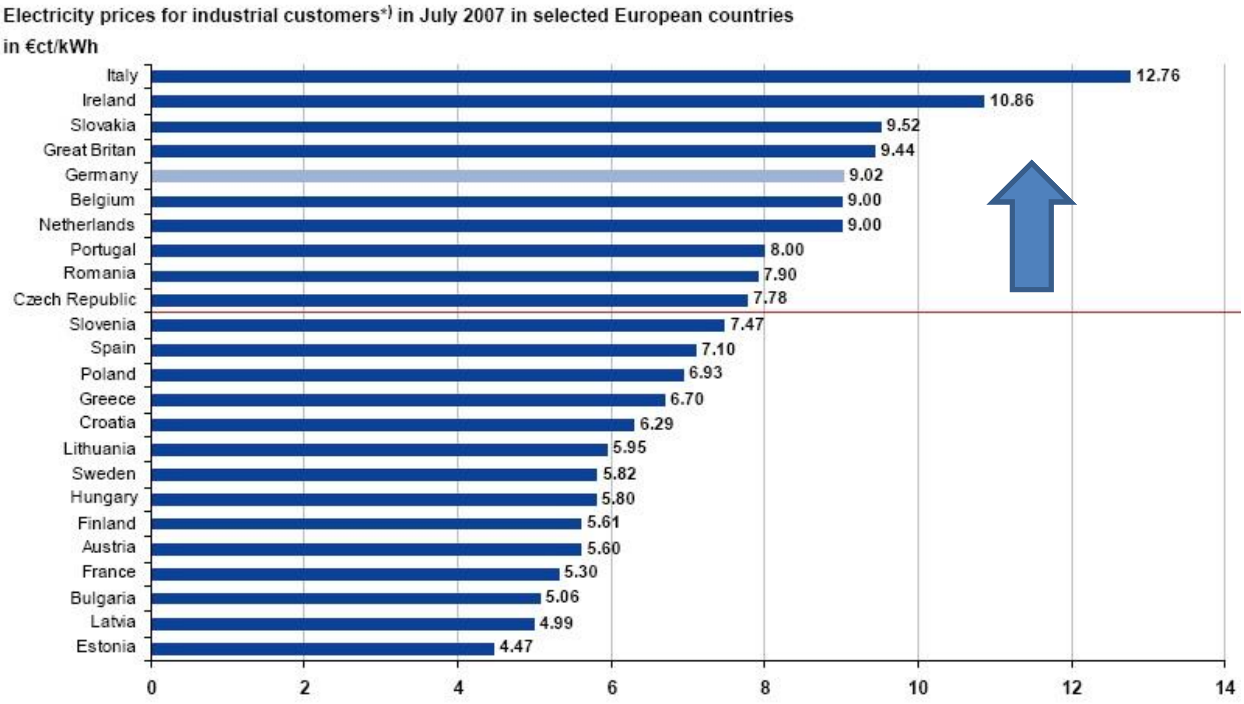

Figure 6-16 European power prices for industrial customers (source: http://rwecom.online-report.eu/factbook/en/marketdata/electricity/supply/electricitypricesineurope.html)

The break-even point for the investment cost of the ORC system depends on the electricity costs and was not assessed in this work package.

Role of false air ingress on the overall performance

False air ingress is one of the major challenges with regard to the application of oxyfuel technology. Basically the thermal energy demand is increased due to the additional heating up of ambient air and the electrical energy demand due to higher necessary performance of the ID fan. In extreme cases the production capacity has to be reduced as the ID fan performance has reached maximum capacity. This circumstance is also valid for conventional operation, for which reason the reduction of the false air is worthwhile already today. In case of oxyfuel additionally the flue gas is diluted causing higher energy demand for the purification of the flue gas for transport, storage or utilization. In this section this circumstance is considered more in detail in terms of total energy efficiency.

Following scenarios have been considered:
For the VDZ process model calculations the false air ingress was defined as (Nm^3/h air ingress) / (Nm^3/h flue gas flow rate out of preheater)

- 4.6% false air ingress: This scenario is based on significant efforts on maintenance in combination with advanced sealing methods.
- 6.3% false air ingress: This scenario is based on significant efforts on maintenance in combination with state-of-the-art sealing measures and marks the reference case.
- 8.1% false air ingress: This scenario is based on improved maintenance in combination with state-of-the-art sealing measures. Experiments in industrial scale plants have proven this level of false air as achievable at high efforts on maintenance.

Table 6-12 Influence of false air on the clinker production process performance

False air case	CO_2 concentration (Flue gas) [%]	Volume flow (Flue gas) [m^3_{stp}/h]	Temperature (Flue gas) [°C]	Enthalpy flue gas + dust [kJ/$kg_{clinker}$]	Energy demand (Clinker burning process) [kJ/$kg_{clinker}$]
4.6 %	80	157,728	390	961	3,114
6.3 %	77	162,813	394	994	3,140
8.1 %	74	170,065	402	1,049	3,182

Table 6-12 illustrates the influence of false air on the performance of the clinker burning process. Due to the above mentioned reasons the thermal energy demand of the clinker burning process rises by 0.8 – 1.3% per 2% of false air compared to the reference case. This is mainly caused by the increasing flue gas enthalpy of 3.3 to 5.5% per 2% of false air. Basically heat introduced in the clinker production process could be recovered in the units preheater and cooler. Especially in the preheater system the energy could only be recovered until a level defined by the capacity stream ratio of gas and material. This means that the additionally added energy due to false air could not be used to preheat the material to calcination temperature on top. This is one factor, why the influence of false air ingress is not a linear but exponential factor, meaning the more false air ingress the higher the influence on the thermal energy demand.

Although false air could also be a source of oxygen for the process, the oxidizer amount could not be reduced as the false air is not controlled provided to e.g. firing locations. That way electrical energy demand could not be reduced. However, the volume flow, the temperature and thus the enthalpy of the flue gas increases due to the increasing of false air ingress. Consequently, there is more heat available for the raw material drying process and power generation with ORC system. But the increase in power output from the ORC system is insignificant. On the other hand not only the volume flow to be treated in the CPU is increased but also CO_2 concentration is reduced, increasing the electrical energy demand. Thus the electrical efficiency of the system with increased power production on the one side and higher energy demand on the other has to be thoroughly balanced.

It is important to note that because of the false air ingress for the oxyfuel process the concentration of N_2 in the flue gas increases to 8%, 10.7% and 13.4%, respectively for 4.6%, 6.3% and 8.1% false air ingress, referring to the total flue gas stream after preheater.
In a comparable oxy-fuel system with the same false air stream ingressing to the process compared to a conventional, air fired system, the missing dilution by N_2 from the combustion air in the flue gas for oxy-fuel combustion increases the percentage of N_2 coming from the false air ingress by a factor of around 2.

Consequently, the main effect of the change in amount of air leak is on the power consumption of the CPU. The specific power consumption of the CPU is 417.7 kJ/kg_{CO2} in the base case with 6.3% air ingress. It decreases to 406.6 kJ/kg_{CO2} in the case of the 4% false air ingress, which represents a 2.7% decrease. As expected the specific energy consumption increases significantly for the 8.1% false air ingress case to 432.1 kJ/kg_{CO2} representing a 3.5% increase compared to the base case with 6.3% air ingress. A base case without any false air ingress in the cooler was also considered. The specific energy consumption in the CPU is reduced slightly to 417.1 kJ/kg_{CO2}.

Another effect is that the CO_2 purity reduces with increasing air leak for 90% CCR. The CO_2 purities are 97.8 vol%, 97.3 vol% and 96.5%vol% for the 4.6%, 6.3% and 8.1% air ingress cases respectively. See Table 6-14 for the operational performance of these cases.

CO_2 reduction potential

Basically the CO_2 capture rate depends strongly on the performance and the used technology of the CPU, as only additional firing for e.g. raw material/fuel drying or unlikely CO_2 leakages to the surrounding could have an influence on the amount of captured CO_2. There is a trade-off between CO_2 capture ratio (CCR) and the CO_2 purity achieved in the CPU for a given feed gas composition. For the base case with 6.3% false air ingress, the feed to the CPU contains 80 vol% CO_2. At 90% CCR, the CO_2 purity obtained is given in Table 6-13 below. For a given feed composition to the CPU, there will also be an optimum CCR with respect to minimum specific energy consumption.

Table 6-13: CO_2 product composition for the base case with 90% CCR

Component	Composition
CO_2	97.28%
Argon	0.35%
Oxygen	0.74%
Nitrogen	1.62%

This project has received funding from the European Union's Horizon2020 Research and Innovation Programme under Grant Agreement No 641185

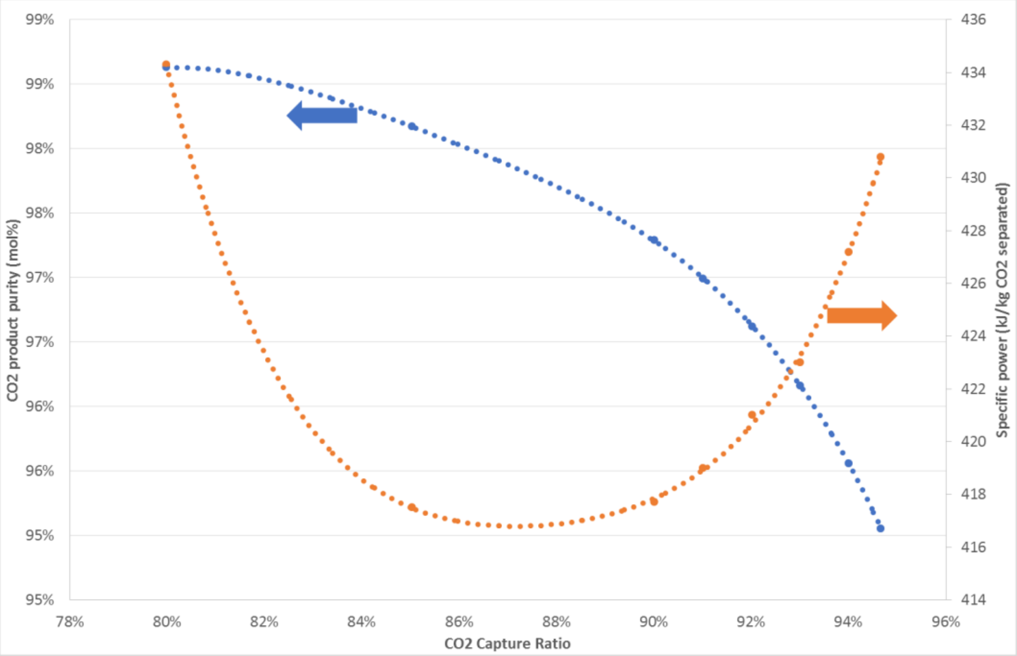

Figure 6-17: Effect of CCR on CO_2 product purity and CPU specific energy consumption

Figure 6-17 shows the variation of CO_2 product purity and specific energy consumption of the CPU with CCR. A maximum of 95% CCR is achievable to ensure at least 95 vol.% CO_2 product purity for the base case. Decreasing the CCR increases the purity and reaches above 99 vol.% CO_2 purity at 80% CCR. As expected, there is an optimal CCR with respect to specific power consumption. The optimal CCR is around 87-88%. However, the curve in the optimmum is pretty flat with no significant change in specific energy consumption between CCRs of 85-90%.

Heat integration model results

A summary of the different cases studied in this work is presented in Table 6-14 and provides the operational performance of the six cases.

Table 6-14: Operational performance of the 6 cases considered

		Base case	4PH	3PH	Low false air	High false air	No false air at cooler
False air	%	6.3	6.3	6.3	4.6	8.1	6
Preheater stages		5	4	3	5	5	5
Clinker production	t/h	125	125	125	125	125	125
Fuel Input	MWth	109	113	118	108	110	109
O_2 flow	t/h	31	31	32	31	31	31
ASU power	MWe	7.0	7.0	7.2	7.0	7.0	7.0
ASU dehydration	MWe	0.53	0.53	0.53	0.53	0.53	0.53
Recycle blower	MWe	0.54	0.55	0.56	0.52	0.54	0.53
CPU power	MWe	11.5	11.7	12	11.2	11.5	11.3
CPU dehydration	MWe	0.6	0.6	0.7	0.7	0.6	0.6
Specific power consumption	kJ/kgCO_2	417.7	418.8	417.1	406.6	432.1	411.1
ORC	MWe	2.9	3.4	5.1	3	2.8	2.9
Net power	MWe	13.2	13	11.8	12.9	13.4	13.1
Cooling duty	MWth	42.7	46.3	50.2	41.2	42.7	42.0
Condenser duty	MWth	15.3	16.9	14.3	14.6	15.3	15.0
Gas recirculation rate	-	0.55	0.55	0.55	0.55	0.55	0.55
CCR	%	90.0	90.0	90.0	90.0	90.0	90.0
CO_2 purity	%	97.3	97.2	97.3	97.8	96.5	97.5
CO_2 captured	t/h	98.8	100.9	103.2	98.9	95.7	98.9
CO_2 emissions	t/h	11.0	11.2	11.4	11.0	10.6	11.0
Specific CO_2 emissions	kgCO_2/t clinker	87.8	89.4	91.3	87.7	85	87.7

7 START-UPS AND SHUT-DOWNS, RECOMMENDATIONS FOR OPERATOR'S TRAINING

The following section provides information about the operation of an oxyfuel kiln based on the above described operational mode determined by process modelling.

7.1 Start-ups under oxyfuel conditions

One of the most important operational steps for the clinker burning process is the start-up of the kiln line. The oxyfuel kiln will be started in conventional air fired case in order to achieve stable conditions, on which basis an appropriate flue gas is generated to be recirculated.

In order to avoid damages at refractories or machinery the kiln system has to be heated up in a defined procedure including precise heating gradients. Meanwhile parameters like temperatures, oxygen levels, emission levels (e.g. CO) and pressure levels (with regard to fan performance) have to be thoroughly observed. After achieving a temperature level of around 1,000°C in the kiln inlet the raw meal supply can be started. Material and fuel supply are stepwise increased until full capacity.

After achieving stable operating conditions, which is defined by target values like:

- Material input and production capacity
- Temperatures (sintering zone 1450°C, calciner 800-900°C)
- Clinker quality in terms of free lime content
- Oxygen level (kiln inlet < 1vol.%, flue gas 3-4 vol.%)
- Emission levels in compliance with emission regulation limits

the oxyfuel mode can be started by gradually replacing ambient air by the oxidizer (O_2 from the ASU) and the recirculated flue gas (Figure 7-1).

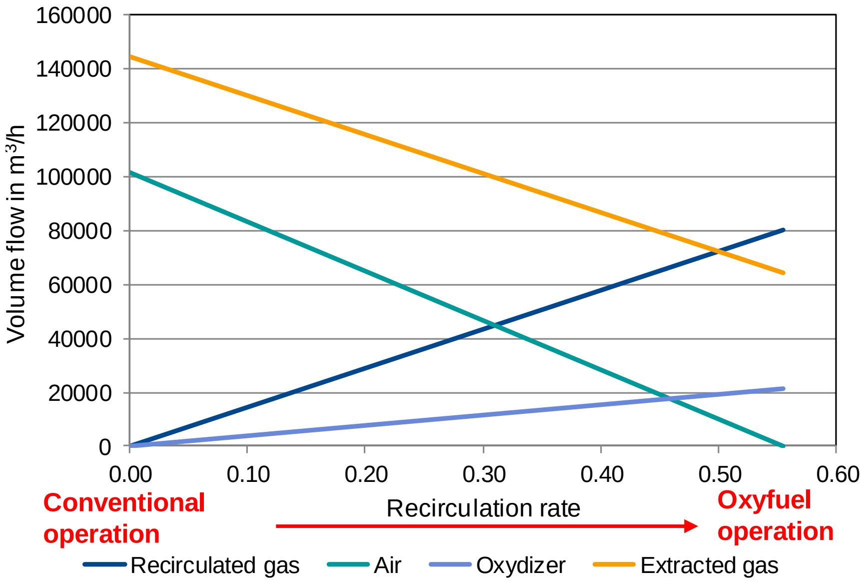

Figure 7-1: Composition of the gas combustion for the conventional air and oxyfuel operation

Figure 7-1 illustrates the dependence between the amount of the recirculated gas, the ambient air, the oxidizer and the extracted gas (either to CPU or stack). Starting on the left side of the diagram at 100% air fired case, no flue gas is recirculated and hence the total amount led to the stack. Increasing the recirculation rate the flue gas is stepwise recirculated instead of being extracted. That way air input is replaced by recirculated gas. In order to provide the necessary oxygen, which is conventionally included in air, oxydizer from ASU is supplied. This stepwise procedure is followed until the oxyfuel operation is completed (on the right side of the diagram). By this switching mode the flue gas composition is steadily changed. After some recirculation circles of the gas in oxyfuel operation the composition should be stabilized. Based on that, the optimal burner configuration (which is very sensitive to changes in kiln atmosphere) can be fine-tuned. After complete stabilization of the oxyfuel mode the CPU can be initiated as otherwise the CPU could not be properly operated at strongly varying conditions.

7.2 Shut-downs under oxyfuel conditions

Shut downs of the cement clinker burning lines occur under different boundary conditions. Usually the clinker production process is constantly operated and only stopped for yearly maintenance stops or due to market reasons. Apart from these planned controlled shut-downs uncontrolled stoppages are common even in well operated plants due to failures (e.g. blockages from incrustation, damages at machinery or failures of energy supply).

In the planned case the clinker production process could be shut down following a controlled procedure. The CPU should be closed, but ensuring a controlled exhaust of the flue gas complying with all emission limits. Afterwards the production could be slowly reduced to void damages at equipment.

In case of uncontrolled stops special attention has to be paid to the controlled extraction of the flue gas to avoid negative effects on the purification or recirculation devices. Most important it has to be ensured that CO_2 rich gas is not leaked out of plant and harm personal and environment. Therefore detailed emergency and evacuation plans have to be available in urgent cases.

7.3 Operator's training

In conventional kiln operation many factors require the supervisors' attention such as heterogeneity of fuels, process fluctuations, burner flame formation and observation of emission limitations. Using recirculation the requirement to manage the process parameters increases, which makes the operation even more difficult. Moreover, additional plant units have to be controlled. In addition the plant and process parameters interact with each other, therefore the risk of losing control of the process becomes higher and as a consequence more safety and controlling devices have to be installed and additional special instructions for personnel is essential. [IEA-13]

In which way control loops can be installed, is still a big issue, which is currently investigated in the ECRA CCS project. E.g. whereas the flame and temperature profile in the kiln is usually controlled by fuel input and burner adjustment, in oxyfuel operation the set-up and control of recirculation rate becomes an additional degree of freedom.

Moreover more control and measuring devices have to be installed as the common way of trouble-shooting like opening of poke-holes and inspection doors are limited due to false air ingress. Up to a certain extent the CPU is capable to handle changes in flue gas composition caused by short-term inspections. Nevertheless the efficiency is limited by these measures.

Furthermore process fluctuations could appear, if certain aggregates are not operated in a proper way. Following additional aggregates causing potential process fluctuation are identified in oxyfuel operation:

Table 7-1 Potential failures in oxyfuel operation

Failure	**Influence on**
Wear of sealings	False air ingress
Cleaning intervals (coating removal)	False air ingress
Malfunction of the condenser	Gas humidity
Flap position of the flue gas separation into recycled and extracted (to CPU) part	Amount of recycled flue gas
Malfunction of the air separation	Oxygen content in oxydizer

Those failures could have different harming potential on the energy demand or even function of plant units, as shown in Figure 7-2 in relation to reference values stated in the Framework document. E.g. if the oxidizer purity drops the energy demand is tremendously increased due to higher necessary gas streams to be heated up and lower CO_2 concentration in the flue gas. On the other hand the risk of occurrence is very low. As already mentioned the false air ingress is more risky for the operation of an oxyfuel kiln.

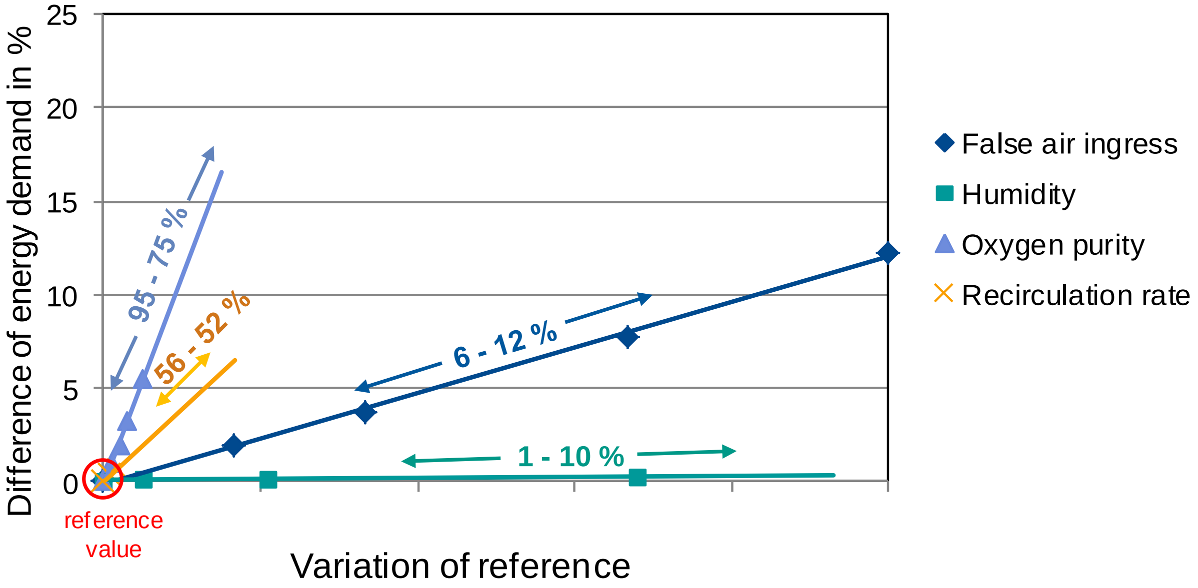

Figure 7-2: Harming potential of process fluctuation on energy demand (based on modelling results)

The additional components and the impact of the false air ingress to the process energy efficiency make the monitoring of the process parameters for the oxyfuel operation more complex than that of the conventional operation. As first step of the training the so-called SOPs (standard operating procedures) for all aspects of the plant like start-ups/shut-downs, maintenance and all possible disturbances have to be developed. Based on that the comprehensive operator’s training should include the following parts:

- Basic theoretical training (e.g. physics, chemistry, process technology)
- SOP based training to increase understanding of the new process
- Simulation of the oxfuel plant to train the operation and the handling of failures
- On-site visits to understand the actual process equipment
- Training on actual plant operation supervised by experienced commissioning engineers

Furthermore the control system includes more safety alerts for uncontrolled leakages due to new hazards caused by handling pure oxygen or CO_2 rich streams in order to protect personal and environment. E.g. due to its high density, CO_2 leaking from clinker cooler chambers could accumulate in the cooler basement and therefore the atmosphere near the cooler is required to be controlled permanently. For detailed information see deliverable D7.1 “Risk assessment of oxyfuel combustion in cement plants”. Therefore supervisors should also be well informed about not only about the new operating modes but especially about all this new hazards and their harming potential.

8 SUMMARY AND CONCLUSION

Before proceeding to the design of a full oxyfuel cement pilot plant (TRL 7) the individual testing (corresponding to reaching TRL 6) of key oxyfuel components (burner, calciner, cooler) were executed in the CEMCAP project based on the theoretical findings from the ECRA CCS project. Especially, testing and demonstrating prototypes of the oxyfuel calciner, clinker cooler and main burner under industrially relevant conditions was undertaken in CEMCAP work packages 7, 8, 9. Due to the counter current flow of material and gases in the clinker production process, changes in the operational parameters in one process unit influence connected equipment units. An assessment of the overall process and the individual units of equipment can be achieved by modelling of the oxyfuel process. For this purpose the VDZ process model was adapted to the oxyfuel process conditions and the outcome of the CEMCAP prototype testing. This included scaling and further evaluation of the comprehensive data from the testing and restructuring the process modules. In combination a heat integration model of SINTEF considered the energetic optimisation of the overall process including CO_2 Purification Unit (CPU) and Air Separation Unit (ASU). The optimisation of the oxyfuel process in the simulations considered different operational modes, which had been investigated in the prototype tests, such as varying material and volume loads, combustion characteristics (flame length and shape), false air ingress and degree of heat exchange. The final optimised oxyfuel process simulation results showed:

- Due to higher calcination temperatures the degree of calcination at kiln inlet has been decreased for equipment protection and to avoid unwanted coating in the calciner.

- The cooler performs even better under oxyfuel conditions due to the increased heat exchange between the hot clinker and the CO_2 rich gas. However, the cold clinker extraction is a focal point for limiting false air ingress to the oxyfuel gas recirculation.

- The heat transfer by radiation from the kiln gas to the material could be matched to the reference air case (BAT3000) by adapting the burner setting. This was achieved by switching mainly oxygen input from secondary to primary gas. Thus the heat transferred to the material in the sintering zone and the temperature profiles along the kiln are optimal to generate the required clinker phases. Furthermore it can be expected that the coating behaviour of the material in the kiln and the thermal load of the rotary kiln are similar in both cases and therefore fulfil a known optimum operational mode.

- Although the area of formation of clinker phases is slightly shifted in the kiln due to changing temperature profiles, a good clinker quality comparable to air-fired case is achieved in the optimised oxyfuel operation.

- In the optimised oxyfuel operation a flue gas could be generated, which consists of 83.4 vol.% CO_2 on a dry basis, which is an adequate level with regard to CPU performance.

Due to the changing gas atmosphere energy is shifted in the clinker production process when applying oxyfuel technology. The oxyfuel gas has higher heat capacity due to higher heat capacity of CO_2 compared to N_2 and transfers more energy with the gas flow. Consequently, more energy input is needed in the kiln and less in the calciner firing. Also, more energy is leaving the plant by flue gas enthalpy. On the other hand waste energy from the clinker cooler recirculation gas is reduced, as CO_2 rich gas can recuperate more energy from the hot clinker in the cooler for the clinker burning process. However, the sum of both streams shows that the available waste heat is about 17% higher than in the air case causing an increase in total energy demand to 3,140 kJ/kg clinker (+3.8% compared to air fired case) .

In order to evaluate the energy demand of the oxyfuel clinker burning process for different operation scenarios the false air ingress and the preheater stages were varied. Based on that the energetic integration of e.g. ASU and CPU have been simulated within the process integration studies of SINTEF. The options for waste heat recovery and the heat integration were evaluated with the help of an iterative procedure between the VDZ process modelling and the SINTEF heat integration modelling.

The simulations showed that the false air ingress and the number of the preheater stages play a significant role in terms of thermal and electrical energy demand for the overall oxyfuel clinker burning process:

Due to the small negative pressure in the kiln system in reference to ambient pressure unwanted false air enters the oxyfuel gas recirculation. A range of 4.6% to 8.1% of false air ingress was assessed. The thermal energy demand of the clinker burning process rises by 0.8 – 1.3% per 2% of false air, mainly caused by the required heating of this additional air. Simultaneously the specific power consumption of the CPU increases by 2.7 – 3.5% per 2% of false air due to the dilution of the flue gas. As the electrical energy demand for the CPU is rising exponentially with increasing false air ingress, the maximum acceptable level is around 8%.

The simulation results of the preheater stage variation has shown that with the consideration of the increased energy consumption of ASU and CPU the efficiency of the additional fuel used in case of a reduction from 5 to 4 and 3 preheater stages are only 5.6% and 15.2%. In conclusion the production of power makes sense, if a surplus of waste heat is available anyway. It is not energy efficient if the very high energy efficiency of the clinker burning process is significantly decreased. But due to the high electricity costs compared to the coal prices or prices for alternative fuels, the above described measure becomes profitable at electricity cost levels of 75 €/MWh (see *Figure 6-16*).

Based on results from the CEMCAP experimental tests of the calciner, burner and clinker cooler under oxyfuel conditions, the simulation results of the oxyfuel clinker burning process were refined, which enabled a detailed investigation about the heat integration and the energy efficiency of the oxyfuel clinker burning process. The simulations of the oxyfuel technology gave a good overview about the operation parameters which differ from that of a conventional plant.

The results confirmed that a retrofit of existing plants is possible. But in order to refine the experimental results and evaluations and for validation of the simulation results and conclusions, experiments at a full scale oxyfuel cement pilot plant (TRL7) will be necessary. Currently, the overall investment costs and the operational costs for further research and development of this technology in a European project are seen as a significant barrier. The required increase in scale and TRL level will depend on the availability of appropriate funding programmes for the investigation of the carbon capture technology and its demonstration in the cement industry.

9 APPENDIX

A.1 Appendix A: Bibliography and references

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