Climate protection is seen as one of the key issues on the international policy agenda. Following the Paris climate agreement in 2015, all signatory states are facing the challenge of reducing their CO₂ emissions significantly. CO₂ emissions from the cement industry amount to 6 to 7% of global anthropogenic CO₂ emissions and there are currently no feasible methods to produce clinker and therefore cement without releasing CO₂ from CaCO₃. A technological option to significantly reduce GHG emissions from the cement industry is CO₂ Capture and Storage/Utilisation (CCS/U). Technologies developed for CO₂ capture at power plants (many of them at Technology Readiness Level TRL7-8) need significant adaptation in order to be applied to cement plants due to different processes and product requirements. When considered for the cement production process, such capture technologies were typically at TRL 4-5 or lower. Therefore, the international research project CEMCAP was realised to bring CO₂ capture technologies for the cement industry to a higher TRL level and thus closer to deployment. The CEMCAP project, which was funded by the European programme Horizon 2020, has focused on investigations on oxyfuel and post-combustion technologies as CO₂ capture technologies for cement kilns. The present paper summarises the research activities focussing on the optimisation of the overall oxyfuel operation of a cement plant via a modelling approach. For the optimisation of the process the VDZ process model, which has already been used in the ECRA CCS project, was adapted to the prototype test results of an oxyfuel cooler, burner and calciner within the CEMCAP project. Moreover, the paper provides information about important operational steps, such as start-up and shut-down procedures of the clinker burning process under oxyfuel conditions.

(English text supplied by the authors)
1 Introduction

Before proceeding to the design of a full oxyfuel cement demonstration plant (Technology Readiness Level TRL 7), the individual testing of key oxyfuel components (burner, calciner, cooler) was performed based on the theoretical findings from the ECRA CCS project.

In 2007 ECRA initiated this international research project as a long-term project with a step-by-step approach, consisting of five consecutive phases. Within phases I and II of the ECRA project, potential CO2 capture technologies were identified, and the applicability to the clinker burning process was evaluated. Phase III of the project, which was carried out between 2009 and 2011, focused on investigations on oxyfuel and post-combustion technologies as CO2 capture technologies for cement kilns. Within the ECRA CCS project phase III a full concept for an oxyfuel cement plant was developed [1]. This oxyfuel model already delivered some preliminary results, which were refined by the results from the prototype tests during the CEMCAP project. 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 and was optimised by including comprehensive data from the testing and restructuring of the process modules.

After the optimisation of the oxyfuel process model, the waste heat recovery and the heat integration were evaluated. In order to evaluate the energy demand of the oxyfuel clinker burning process for different operational scenarios, the VDZ process model was applied under six different operational conditions in which the false air ingress and the preheater stages were varied.

2 Oxyfuel technology

Oxyfuel technology for CO2 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 it being supplied to the kiln for the combustion process. After the oxyfuel combustion and calcination process the concentration of carbon dioxide in the flue gas is increased significantly. To maintain an appropriate flame temperature, part of the CO2-rich flue gas has to be recycled while the oxygen concentration in the combustion air and the combustion temperature are adjusted by the recirculation rate. As a consequence of the CO2-enriched atmosphere in the kiln system (exceeding minimum 70 vol. %), only a comparatively simple carbon dioxide purification is required for the CO2 capture from the flue gas cycle. As part of carbon capture and storage/utilization technology the purified CO2 stream is discharged to a compression facility and then delivered to a transport system [2, 3].

2.1 Oxyfuel process layout

The principal configuration of an oxyfuel cement plant leaves the conventional plant unchanged in most aspects. The main additional installations required for the oxyfuel kiln are:

- Rotary kiln burner for oxyfuel combustion
- Oxyfuel clinker cooler (e.g. recirculating cooling)
- Exhaust gas recirculation system
- Gas-gas heat exchanger
- Condensing unit
- Air separation unit (ASU)
- CO2 purification unit (CPU)
- Optimised sealings compared to a conventional plant

The relevant changes to the clinker production process are illustrated in Fig. 1.

2.2 Oxyfuel modelling and optimisation

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 existing VDZ process model already used in the ECRA CCS project [7] was adapted to the oxyfuel process conditions and the outcome of the prototype testing, which was conducted in the CEMCAP project [6, 5, 9]. In addition, a heat integration model was used at SINTEF to evaluate the energetic optimisation of the overall process including the power-intensive CPU and ASU.

Figure 1: Scheme of the oxyfuel cement plant, based on ECRA CCS and the CEMCAP project results [8]
Basically, applying oxyfuel operation to the clinker burning process affects the operational conditions as well as the material conversion due to the different gas properties of the burning atmosphere. Previous studies already proved the energy shifting (from kiln hood to the kiln inlet) in the clinker burning process due to different heat capacities and heat radiation properties of CO₂-dominated atmospheres [2]. The mineralogical clinker phase formation is mainly influenced by the resulting shifts of the temperature profiles in the kiln. Whereas, the calcination reaction is directly affected by the higher surrounding CO₂ partial pressure, which leads to an increased equilibrium temperature of the reaction [6, 1]. Based on these previous findings and the CEMCAP prototype tests, the modelling of the oxyfuel operation could be refined and further optimised:

- Due to higher calcination temperatures the degree of calcination at the kiln inlet was slightly decreased for equipment protection and avoidance of excessive coating formation.
- The cooler performed even better under oxyfuel conditions due to the higher heat capacity of CO₂ and thus increased heat exchange between the hot clinker and the CO₂-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 for the oxyfuel operation could be matched to the air-fired operation by adapting the burner settings. This was achieved by switching mainly oxygen input from secondary to primary gas.
- 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 the air-fired operation was achieved in the modelling of the optimised oxyfuel operation (Fig. 2).
- In the optimised oxyfuel operation a flue gas could be generated which consists of 80 vol. % CO₂ on a dry basis, which is an adequate level with regard to CPU performance for CO₂ concentration to levels between 95 and 99 vol. %.
- For the optimised oxyfuel operation the feed to the CPU contains 80 vol. % CO₂. With respect to the specific power consumption of the CPU (kJ/kg CO₂ separated) an optimal CO₂ capture ratio (CCR) around 85 to 90 % was calculated. The CO₂ product purity is calculated at up to 973 %.

Due to the described energy shift more energy leaves the plant by flue gas enthalpy. On the other hand, waste energy from the clinker cooler recirculation gas is reduced, as CO₂-rich gas can recover more energy from the hot clinker in the cooler for the clinker burning process. However, the sum of both streams shows that due to the energy shift to the kiln inlet the available waste heat is about 17 % higher in the oxyfuel operation than in the air-fired operation, causing an increase in total energy demand of 3.8 % compared to air-fired operation.

In order to evaluate the energy demand of the oxyfuel clinker burning process for different operation scenarios, the false air ingress and the number of preheater stages (influencing the available waste heat) were varied. Based on the kiln and preheater process modelling by VDZ, the energetic integration of e.g. ASUs and CPUs were modelled within the heat integration studies of SINTEF [8]. In summary, the following results were obtained:

- The thermal energy demand of the clinker burning process rises by 0.8 to 1.3 % per 2 % of false air, mainly caused by the required heating of this additional air. Simultaneously, the specific electrical energy demand of the CPU increases by 2.7 to 3.5 % per 2 % of false air due to the dilution of the flue gas. This clearly shows the need for greater efforts with regard to sealings.
- With respect to CO₂ emissions, the energy efficiency and the production of electrical energy for the oxyfuel clinker burning process, the modelling results showed that decreasing the number of preheater stages and increasing the fuel flow and heat available in the system is not an efficient option with regard to the reduction of CO₂ emission.

3 Start-ups/shut-downs under oxyfuel conditions

Considering the operation of an oxyfuel cement kiln, start-ups/shut-downs have to be taken into account. The oxyfuel kiln will be started in a conventionally air-fired mode in order to achieve stable air operation, from which flue gas is generated to be recirculated. Afterwards, the oxyfuel operation can be started by gradually replacing in the firing the ambient air by a mix of recirculated flue gas and the oxidizer (O₂ from the ASU).

In this switching mode the flue gas composition is steadily changed. After some recirculation circles of the gas in oxyfuel operation the gas composition in the kiln system will become stable. The optimal burner configuration is very sensitive to changes in the kiln atmosphere. It can be fine-tuned according to the conditions of oxyfuel operation [5]. Only after complete stabilisation of the oxyfuel operation the CPU can be initiated, as otherwise the CPU could not be properly operated at varying conditions.

Planned, controlled shut-downs (e.g. for yearly maintenance) can follow common operational procedures, starting with

![Figure 2: Clinker minerals formation along the kiln for air and oxyfuel operation conditions](image)
closing the CPU and a controlled release of flue gas complying with all emission limits. In the case of uncontrolled, unforeseeable kiln system 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 importantly, it has to be ensured that CO₂-rich gas does not leak out of the plant and harm personnel, the plant neighbourhood or the environment.

3.1 Kiln control and operational procedures
Already in conventional kiln operation many factors require the supervisors’ attention. An oxyfuel kiln system with flue gas recirculation and integration of additional plant units requires an advanced management of the process. Additional special instructions for personnel are essential [3] and supervisors and operators have to be trained adequately. As plant and process parameters interact with each other, the risk of losing control of the process becomes higher and as a consequence more safety and controlling devices have to be installed. Also, more control and measuring devices are required as the usual ways of trouble-shooting such as opening of poke-holes and inspection doors are limited by the need to minimize false air ingress. The control system will include more safety equipment for detecting and preventing any gas leakages in order to protect personnel and the environment from new hazards which originate from handling pure oxygen or CO₂-rich gas streams. Strategies for installation of control loops are currently investigated in the ECRA CCS project.

4 Final remarks

Based on results from the CEMCAP project prototype tests of the calciner, burner and clinker cooler under oxyfuel operation conditions and their experimental results, the process modelling of the oxyfuel clinker burning process was refined. The combination with a heat integration model also enabled a detailed investigation of the energy efficiency of the oxyfuel clinker burning process. By adaptation of the process parameters such as burner setup, calcination temperature shift and enhanced cooling rates, the oxyfuel clinker burning process could be optimised to counteract the effect of energy shift for oxyfuel operation. The CO₂ capture rate of the modelled oxyfuel process was determined as between 85 to 90 % at 97 % product (CO₂) purity.

As the electrical energy demand for the CPU rises exponentially with increasing false air ingress the requirement for regular maintenance is much higher for the oxyfuel clinker burning process than for the clinker burning process with air operation. With the results obtained in the CEMCAP project, the Technology Readiness Level (TRL) of the oxyfuel CO₂ capture key technologies for the cement industry reached a higher level (TRL 6). It was confirmed that a retrofit of oxyfuel capture technology to existing plants is possible. The next step is the demonstration of the complete oxyfuel system in cement plants (TRL 7 and 8). The project development [4] and further investigations are ongoing with the aim to achieve the availability of oxyfuel capture technology for deployment in the cement industry before or by 2030.

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