Technical Report

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ECRA CCS Project – Report on Phase III
Table of Contents

1 Executive Summary .......................................................................................................................... 5
2 Introduction ...................................................................................................................................... 7
3 Current Status of CCS .................................................................................................................... 8
  3.1 CCS Roadmaps and ongoing CCS projects ............................................................................. 8
  3.2 Limits and barriers for CCS projects ...................................................................................... 10
4 Principal possibilities for CO₂ reduction in the cement industry .................................................. 12
  4.1 CCS Roadmaps for the Cement Sector .................................................................................. 12
  4.2 CCS Activities in the Cement Sector ..................................................................................... 13
5 The ECRA CCS Project .................................................................................................................. 15
  5.1 Overview .................................................................................................................................. 15
  5.2 Phase I and Phase II ................................................................................................................ 15
  5.3 Research Objectives for Phase III .......................................................................................... 16
6 Oxyfuel Technology ....................................................................................................................... 18
  6.1 General Update ......................................................................................................................... 18
    6.1.1 State of the Art .................................................................................................................. 18
    6.1.2 Preconditions for the Oxyfuel Work Packages ................................................................ 20
  6.2 Full Oxyfuel Technology .......................................................................................................... 21
    6.2.1 Product Quality and Refractory Durability Aspects .......................................................... 21
    6.2.1.1 Clinker and Cement Quality under Oxyfuel Conditions .............................................. 22
    6.2.1.2 Optimisation of the Refractory Lining in Oxyfuel Operation of a Rotary Cement Kiln 27
    6.2.1.3 Product Quality and Refractory Durability .................................................................. 34
    6.2.2 Flue Gas Aspects ............................................................................................................... 35
    6.2.2.1 Optimised Sealings ...................................................................................................... 35
    6.2.2.2 General Layout of a Flue Gas Conditioning Facility for Oxyfuel Operation ............... 41
    6.2.2.3 Evaluation of Flue Gas Aspects .................................................................................... 46
    6.2.3 Design Aspects .................................................................................................................... 47
    6.2.3.1 Burner Design for Oxyfuel Operation ......................................................................... 47
    6.2.3.2 Two-stage Cooler Design for Oxyfuel Operation of a Rotary Cement Kiln ............... 54
    6.2.3.3 Evaluation of Design Aspects ....................................................................................... 60
    6.2.4 Operational Aspects .......................................................................................................... 61
    6.2.4.1 Process Simulation of a Rotary Cement Kiln under Oxyfuel Conditions ...................... 61
    6.2.4.2 Evaluation of Operational Aspects ............................................................................... 72
    6.2.5 Retrofitting Aspects ............................................................................................................ 73
    6.2.5.1 Development of an Overall Concept ........................................................................... 73
    6.2.5.2 Cost Estimation ............................................................................................................ 75
    6.2.5.3 Evaluation of Retrofitting Aspects .............................................................................. 75
6.3 Partial Oxyfuel Technology .................................................................................. 76
6.3.1 Operational and Plant-specific Aspects ............................................................... 76
6.3.2 Retrofitting aspects concerning partial oxyfuel technology .......................... 81
6.3.3 Partial Oxyfuel Operation in Techno- economical Comparison to Full Oxyfuel Operation ................................................................. 82

7 Post-combustion Technologies ............................................................................... 85
7.1 General update .................................................................................................... 85
7.1.1 State of the art ..................................................................................................... 85
7.1.2 Findings from ECRA CCS project phase II ...................................................... 86
7.2 Simulation of amine-based absorption process .................................................. 86
7.2.1 Mathematical model .......................................................................................... 86
7.2.2 Technical realisation ........................................................................................ 87
7.2.3 Verification and results .................................................................................... 88
7.2.4 Conclusion ......................................................................................................... 89
7.3 Laboratory experiments on absorbent degradation .............................................. 90
7.3.1 Experimental set-up ......................................................................................... 90
7.3.2 Results ............................................................................................................... 92
7.3.3 Conclusion ......................................................................................................... 95
7.4 Brevik project ....................................................................................................... 95
7.4.1 Concept study .................................................................................................... 96
7.4.2 Pre-engineering ................................................................................................. 97
7.4.2.1 Flue gas characteristics ............................................................................... 98
7.4.2.2 Flue gas tie-in and monitoring ....................................................................... 98
7.4.3 Selected CCS techniques .................................................................................. 99
7.4.3.1 Amine scrubbing .......................................................................................... 99
7.4.3.2 Chilled ammonia .......................................................................................... 100
7.4.3.3 Carbonate looping ....................................................................................... 100

8 Summary .............................................................................................................. 101

9 Literature ............................................................................................................ 104
1 Executive Summary

The technical potential to reduce overall CO$_2$ emissions from cement manufacturing with today’s technology is limited. In this context the capture of carbon dioxide and its geological storage, often referred to as “carbon capture and storage” (CCS) is seen today as an emerging technology capable of reducing CO$_2$ emissions significantly. According to different CO$_2$ abatement scenarios and the International Energy Agency’s Roadmap, the cement industry is expected to contribute to CO$_2$ mitigation globally by a set of different measures among which CCS plays a key role.

Against this background ECRA has decided to investigate the capture of carbon dioxide as a prerequisite for the safe geological storage of CO$_2$. ECRA’s goal is to examine the technical and economic feasibility of this technology as a potential application in the cement industry.

ECRA’s CCS project is a long-term research project which started in 2007 and comprises five phases. Phases I and II have been completed in previous years. The current report summarises the research results from Phase III in which two major CCS technologies were investigated with respect to their application in the cement industry, namely the amine-based post-combustion carbon capture and the oxyfuel combustion process. Several work packages were defined and assigned to external project partners who carried out the related research work. The possible impact on the cement production process was evaluated as well as questions concerning the CO$_2$ processing, plant integration and energy efficiency.

Oxyfuel technology involves the combustion of fuels with pure oxygen in combination with the recycling of flue gas to moderate the temperature profile. As a consequence of this, both the material conversion in the kiln system and the operational specifications of the overall process are different from those in conventional kiln operation. However, the research in the current phase has shown that the negative impacts of oxyfuel combustion on the product quality seem to be negligible: Different clinkers were burned under oxyfuel conditions in a laboratory oven and were used for the production of cement samples. The testing of the cement characteristics showed only slight variances (below 3 %) in properties like strength development and compressive strength compared to standard cements.

With respect to the temperature profile and gas atmosphere in an oxyfuel kiln the durability of basic and non-basic refractory material under oxyfuel conditions was investigated. Brickwork consistent with basic material withstood the modified burning atmosphere, while the non-basic material showed a higher degree of thermo-chemical attack during oxyfuel treatment.

The electric energy consumption for oxyfuel operation underlined the CO$_2$ purification unit (CPU) as a major cost factor, and that false air ingress becomes an important factor for the CPU performance. A techno-economic analysis looked at different levels of false air. Basically, varying the input CO$_2$ purity in the relevant range of false air resulted in a lower cost increase than enhancing the output CO$_2$ purity for transport and storage to 99%. Nevertheless, suitable concepts for sealing optimisation have to be developed. An improved maintenance of e.g. poke holes or inspection doors was identified as a potentially sufficient measure in terms of improving the CPU performance.

From an operational point of view oxyfuel operation requires an adaptation of the burner design to establish flame characteristics comparable to those under conventional conditions.
Another notable feature of the plant layout is the two-stage clinker cooler. The required gas-tightness of the two stages, which are operated with different gas atmospheres, could be matched by two possible design concepts. Both concepts rely on the separation of the stages by dynamic devices in the hot clinker zone. With reference to a potential retrofit, a concept using two heat shields has been selected as the most promising solution. It has emerged that even existing coolers could be modified with respect to two compartments separated by a separating flap between the part cooled by recycled CO$_2$ and the other being cooled by ambient air.

For post-combustion carbon capture the most common technique is based on amine scrubbing. Two work packages focused on the general equipment dimensioning and possible degradation reactions of the CO$_2$ solvent. Two additional work packages focused on the development and design of pilot plant tests.

Based on numerical process modelling, the dimensions of the necessary absorption column were calculated to about 20 m in height. For a 3,000 tpd clinker kiln, a column diameter of about 6 m would be necessary.

Investigations on the amine degradation reactions have shown a moderate impact of flue gas impurities on the solvent stability. SO$_2$ concentrations should be kept below 10 ppm in an amine-based system. Other flue gas components and impurities did not show a critical impact on the solvent stability.

A concept study and subsequent pre-engineering study were conducted for a post-combustion test facility in a cement plant. The facility was designed to feed up to three pilot scale CO$_2$ capture plants with approximately 0.5 % of the cement plant’s flue gas stream in parallel. The design, construction and operation of the pilot plants and all interfaces between the cement plant and the pilot test facility were defined. All relevant aspects were laid down in a design basis document, providing the basis for potential detail engineering at a later stage.

In conclusion, the findings of phase III have provided answers to important questions which had so far been open. It was confirmed that post-combustion might be available at a given time. Oxyfuel technology would still require more research, even if it could be shown that it might be applicable at existing kilns, however not without major investments. Although this technology might be less expensive than post-combustion, the overall cost due to the investment for modification and the high energy cost once in operation leave the economic impact of CCS on the cement industry as open as before.
2 Introduction

Climate protection is seen as one of the most important items on the worldwide agenda. All states are facing the challenge of reducing their CO₂ emissions significantly, focussing on the major CO₂ sources in order to contribute to the reduction targets being worked out in many countries as well as on a global level. To reach these targets, a portfolio of different reduction measures is seen to be required, including CCS, the capture of carbon dioxide and its geological storage, often referred to as “carbon capture and storage” (CCS).

Different roadmaps including in particular those on CCS have been published recently [IEA, 2009]. They foresee that the cement industry has to contribute to CO₂ mitigation by a set of measures, among which CCS is seen as indispensable. Consequently these road maps point out the need for demonstration projects, implying that after 2020 CCS technologies are expected to be commercially applicable in the OECD countries, and to a significant extent in emerging countries like China and India.

Against this background the European Cement Research Academy (ECRA) has decided to look at the capture of carbon dioxide as a prerequisite for the safe geological storage of CO₂. ECRA’s goal is to examine the technical and economic feasibility of this technology as a potential application in the cement industry. ECRA lays a strong emphasis on the global perspective of its research and also on its sustainability aspect.

In 2007 ECRA initiated its international research project as a long-term project with a step-by-step approach, consisting of five consecutive phases. Within phase 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. The research work was organized into 12 work packages which were assigned to different contractors like research institutes, engineering companies, equipment suppliers and technology providers. The work packages included theoretical work such as process modelling and engineering studies, but also laboratory and small-scale investigations.

The present report summarises the research activities which were carried out in phase III and concludes with a summary and an outlook to phase IV of ECRA’s long-term project.
3 Current Status of CCS

3.1 CCS Roadmaps and ongoing CCS projects

According to the Intergovernmental Panel on Climate Change (IPCC), at least a 50% reduction of global CO2 emissions by 2050 is required to limit the most adverse effects of climate change and to limit the expected temperature increase to less than 2 degrees. The following Figure 3–1 shows the International Energy Agency’s (IEA) so-called BLUE Map Scenario, indicating that CCS has to contribute almost 20% to the required CO2 reduction by 2050.

![BLUE Map Scenario with portfolio of reduction measures](image)

The International Energy Agency [IEA, 2009a] has taken a leading position in the development of low-carbon energy technology roadmaps, including both demand-side and supply-side technologies. Three of those roadmaps are (amongst other things) related to the application of CCS technologies, namely the Technology Roadmap Carbon Capture and Storage [IEA, 2009a], the Technology Roadmap Carbon Capture and Storage in Industrial Applications [IEA, 2011], the Cement Technology Roadmap 2009 (see also chapter 3.1) [IEA, 2009] and others [IEA, 2008-1; IEA, 2010].

The Carbon Sequestration Leadership Forum [CSLF, 2011] and the Global CCS Institute [GCCSI, 2009; GCCSI, 2011] regularly issue reports about ongoing CCS activities and identify gaps which could endanger the achievement of objectives. The Carbon Sequestration Leadership Forum also issues Technical Roadmaps on CCS which are updated regularly [CSLF, 2011] and give an overview of the ongoing worldwide CCS activities of current (operational and planned) CCS projects and general CCS activities.
The Global CCS Institute (GCCSI) keeps a list of large-scale integrated CCS projects which have been identified around the world. The list is published on the GCCSI website (see “www.globalccsinstitute.com”) and regularly in the Carbon Capture Journal [CCJ, 2012]. Currently 78 projects are listed, but only 8 of them are in operation. The majority of them are EOR (Enhanced Oil Recovery) projects in oil producing countries.

The European Union is funding full-scale and full-chain (including capture, transport and storage) CCS projects under the European Energy Program for Recovery (EEPR).. Six projects have signed grant agreements in 2009/10, namely Jänschwalde (D), Hatfield (GB), Porto Tolle (I), Rotterdam (NL), Belchatów (PL), Compostilla (E). However, as the European CCS Directive has not been transposed into the national legislation in most member states hosting a CCS demonstration project, legal uncertainty still remains. As a result of this, the Jänschwalde demonstration project was recently stopped and a total investment of 1.5 billion € was put on hold. At this time only the Rotterdam project is likely to be operational by 2015.

Other planned demonstration projects like the Longannet CCS project at a coal-fired power station in Scotland were also cancelled recently. The reasons might be slightly different from case to case but they all have in common a lack of public acceptance and a pending legal framework.

In the forthcoming years, European CCS projects can also be funded through financial means from the NER300 programme (New Entrants Reserve) under the Emissions Trading Scheme. A wide range of different CCS technologies is covered by this funding programme. Depending on the outcome of the first round of the NER300 call, 3–6 CCS projects (in total up to 8 CCS projects) could be included and could be operational by 2016/17. A potential demonstration project at a cement kiln would only be eligible for funding if it would capture and store 500,000 t CO2 per year.

Apart from potential demonstration projects more than 30 small-scale CO2 capture pilot projects are in operation in the power sector [GCCSI, 2011].
3.2 Limits and barriers for CCS projects

CCS is certainly a technology which – due to the expected cost - will have a strong impact on any industry in which it is applied. Today, the costs for carbon capture are expected to be still very high and in the range between 40 and 100 € per t of CO₂, not taking into account additional costs for CO₂ transport and storage. An overview of current estimates of CCS costs was recently compiled by the ZERO Emission Platform [ZERO, 2011], [STR, 2011].

While the objective of ongoing research projects is certainly to optimise the CO₂ capture technologies and to reduce the CO₂ capture costs, the question of whether at a given time CCS might be cost-competitive compared with other low-carbon energy technologies still remains open.

Regulatory frameworks for CCS projects are still pending, key questions concerning e.g. licensing and permitting procedures, monitoring, long-term liability and risk management of storage sites, pipeline access, etc. are open. In the European Union, the CCS Directive [CCSD, 2009] is intended to provide the legal framework for CCS projects. The Directive had to be implemented in the national legislation of the individual member states by the end of June 2011. However, at the end of 2011 only two member states (Spain and Romania) had met their obligation, which underlines the basic lack of public acceptance for CO₂ storage.

This is also the case for CO₂ transport. A pipeline network would be the most appropriate system for the transport of relevant amounts of CO₂. Ship transport could be an alternative if the emission source is located close to a waterway or close to the coast. The transport of CO₂ by rail or by trucks would only make sense for small volumes of CO₂. Up to now, there is no CO₂ transport infrastructure available in Europe. In the United States a pipeline network for CO₂ transport is in operation (> 5,000 km). The existing long-term experience has shown that these pipelines can be operated safely.

Due to the limited CO₂ pipeline infrastructure, there are only few specifications regarding the purity of the compressed CO₂ gas stream. However, the separation of impurities in the CO₂ would significantly affect the costs of the CO₂ capture technologies. A report about this important issue was published by the IEAGHG with support from the Global CCS Institute (GCCSI) [IEAGHG, 2011].

Finally it is not clear how CO storage can be managed not only in large scale application but even for demonstration projects. According to the existing CCS roadmaps, the so-called BLUE Map scenario would require 1.2 Gt of CO₂ storage capacity in 2020 and 145 Gt of worldwide CO₂ storage capacity in 2050. In principal, captured CO₂ can be stored in different types of underground storages, like saline aquifers, depleted oil or gas fields or coal seams. The oil and gas industry has used CO₂ injection and storage for more than 40 years (Enhanced Oil Recovery, EOR) and long-term experience in CO₂ is available e.g. from the Sleipner project (~ 1 Mio. t CO₂/a) and the Snøvit project (~ 0.75 Mio. t CO₂/a) in Norway, the Weyburn project (2.7– 3.2 Mio. t CO₂/a) in Canada or the In-Salah project in Algeria (1.2 Mio. t CO₂/a).

In Europe, two major research projects (GESTCO, GeoCapacity) have been carried out to identify and characterise potential CO₂ storage sites and to assess the European capacities for the storage of CO₂. Based on this an atlas of European CO₂ storage sites has been developed. For central and northern Europe, the North Sea could offer significant storage capacities, but up to now there is no concept for an appropriate CCS infrastructure.
So-called mineral sequestration has been discussed as a potential storage mechanism [ZEV, 2011] in which minerals like olivine and serpentine in underground geological formations were suggested to absorb huge amounts of captured CO₂. However, this type of CO₂ sequestration would need large deposits of those minerals in the vicinity of the emission sources and would furthermore require large mining activities. In addition the corresponding chemical reaction turns out to be very slow, making the whole process even more difficult from a practical point of view.

With respect to public awareness and acceptance of CO₂ capture and storage a survey which was carried out in several European countries showed that only a small percentage (10 %) of the European population is aware of the concept of carbon capture and storage for climate protection [SEB, 2011]. In this context, the storage of CO₂ is highly controversial in the public discussion. As a result of this, the exploration of storage sites, which had been started in connection with planned demonstration projects, was stopped in several cases due to public resistance.
4 Principal possibilities for CO₂ reduction in the cement industry

The cement industry has various options to reduce CO₂ emissions from the cement production process. Several reports have summarised the principal possibilities to reduce the specific CO₂ emissions [YOU, 2011; PCA, 2008; ZHU, 2011; BOS, 2009; BAR, 2009; BAL, 2009; HOENIG, 2011b], which are:

– utilisation of low-carbon raw materials - limited potential
– utilisation of alternative (CO₂ neutral) fuels - applied already in many plants with remaining potential on a global scale
– production of new cement clinkers - in research today
– production of cements with low clinker/cement ratios - applied already in many plants with remaining potential on a global scale
– improving the energy efficiency of the cement production process - only limited potential left
– application of carbon capture technologies - in research today

The overall potential of these measures strongly depends on the ones which are not yet available today. In this context many roadmaps see CCS as an essential CO₂ mitigation measure, even if this technology is far from being applied for technical and economic reasons.

4.1 CCS Roadmaps for the Cement Sector

The International Energy Agency and the CSI (Cement Sustainability Initiative) member companies have cooperated to develop a roadmap for the cement sector for carbon emissions reductions up to 2050 [IEA, 2009], [WBCSD, 2010]. According to this roadmap, the cement industry would have to contribute significantly to the required CO₂ reduction rates in the years to come. The major part of the reduction efforts is seen as being provided by the application of CCS technologies (see Figure 4–1). In 2050, around 50% of all cement kilns in Europe, North America and Australia are to be equipped with carbon capture technologies, and in addition 20% of the kiln lines in China and India.

In 2011, the United Nations Industrial Development Organization (UNIDO) in cooperation with the IEA published a new roadmap on CCS in industrial applications [IEA, 2011]. According to this, the cement industry is seen to have the potential to capture 500 Mio. t/y of CO₂ in 2050 by the application of CCS technologies (see Figure 4–2).

While the overall technical feasibility is still open it is obvious even today that the estimated costs for CCS application in the cement industry will be extremely high. From today’s view, cement production costs would roughly double.
4.2 CCS Activities in the Cement Sector

Up to now, quite a few CCS activities are taking place or have taken place in the cement sector. All projects are pre-pilot scale; an overview can be given as follows:

- The Australian Organisation CO2CRC (Cooperative Research Centre for Greenhouse Gas Technologies) explored the opportunities for the application of CCS technologies in...
the cement industry [PUY, 2009]. However, no further CCS studies or investigations in the cement sector have become known since then.

– The Institute of Energy Systems at the Hamburg University of Technology (TUHH) is carrying out an industry funded research project “Potential of CCS Technologies for Reducing CO₂ Emissions in Cement Production”. In particular, process simulation studies about the application of oxyfuel and post-combustion technologies at the clinker burning process are being carried out.

– The Spanish organisation CIUDEN (Fundación Ciudad de la Energía) operates a Technology Development Centre for CO₂ capture. Currently a research project is being carried out on oxycombustion in a 30 MW Circulating Fluidized Bed (CFB) boiler. Apart from this, CIUDEN is planning to extend its oxyfuel research into other industrial sectors like the cement industry. In this context, CIUDEN and Oficemen, the association of Spanish cement producers, have started an initial dialogue on the construction of a small-scale oxyfuel-fired cement kiln. However, it is not clear if funding means would be available or if other institutions or companies from the cement sector would cooperate.

– At the University of Zaragoza, studies have been carried out about the symbiosis of power plants, cement plants and CO₂ capture systems. The calcium looping process was identified as a promising technology for CO₂ capture as an economically attractive option [ROM, 2011].

– At the beginning of November 2011, it was reported that the Taiwanese Industrial Technology Research Institute (ITRI) and Taiwan Cement, the largest cement producer in Taiwan, had signed a letter of intent to cooperate in a joint CCS project. Details about the size of the project and the carbon capture technology have not been disclosed up to now. It was reported that small-scale trials have already been started at the Hualien cement plant [TAI, 2011].

– In the United Kingdom, studies on carbon capture at cement kilns have been carried out at university level. In particular the potential of the calcium looping process was investigated at the University of Edinburgh [CAN, 2011] and the Imperial College in London [DEAN, 2011].

– Cemex USA planned to carry out a CCS demonstration project (CO₂ capture with dry sorbents and subsequent sequestration) in its Odessa Plant [NAR, 2011]. The first phase of the project was funded by the U.S. Department of Energy (DOE) / National Energy Technology Laboratory (NETL). It was planned to design a commercial-scale plant with dry sorbent CO₂ capture and subsequent compressing and storage facilities. The capacity of the plant was to be up to 1 Mio. t CO₂ per year. However, after completion of the first phase the project was cancelled due to financial and technical reasons.

– At the beginning of 2010, it was reported that the Texas based company Skyonic had won a grant to the amount of 3 Mio. US-$ from the US Department of Energy (DOE) for an industrial carbon capture project. The project was to be carried out at Capitol Aggregates Ltd., a large cement plant in Texas [JON, 2011]. With the so-called SkyMine® process, CO₂ emitted from industrial flue gases is captured and mineralised to marketable products like sodium bicarbonate. The current state of the project is not clear.
5 The ECRA CCS Project

5.1 Overview

The ECRA CCS project was started in 2007 to examine the technical and economic feasibility of this technology. It was set up as a long-term project which comprises five phases:

Phase I: Literature and scoping study (January - June 2007) finalised
Phase II: Study about technical and financial aspects of CCS projects, concentrating on oxyfuel and post-combustion technology (summer 2007 - summer 2009) - finalised
Phase III: Laboratory-scale / small-scale research activities (autumn 2009 - autumn 2011) - finalised
Phase IV: Pilot-scale research activities (time frame: 2 - 3 years)
Phase V: Demonstration plant (time frame: 3 - 5 years)

Each of the phases requires the deliverables of the previous phases. Phases I, II and III have been completed [ECRA, 2007; ECRA, 2009; HOENIG, 2011a] - the present report summarises the results from phase III. The further course will be decided in the first quarter of 2012. Based on the outcome of phase III, ECRA will decide if and how to proceed with phase IV.

5.2 Phase I and Phase II

Phase I of ECRA’s CCS project was finalised in summer 2007 and provided a first overview of CCS and its potential implications which can be envisaged for the cement industry. It includes an evaluation of the pros and cons of potential application in the cement industry. Ultimately, four options to capture CO₂ were examined, which are currently being discussed: pre-combustion, post-combustion, oxyfuel technology and carbonate looping. Although a detailed technical understanding of CCS is still pending, the study concluded that all capture technologies are today far from being applicable to the cement industry due to technical and cost reasons.

Nevertheless, some capture technologies seem to be more appropriate for potential application at cement kilns than others. This applies to oxyfuel and post-combustion (chemical absorption) technologies. Consequently ECRA decided to continue the project and launch phase II in order to investigate these technologies in more detail in a feasibility study.

Phase II started in the second half of 2007 and was completed in summer 2009. The main objective of this phase was to perform a more detailed study for CO₂ capture at the clinker burning process focussing on oxyfuel and post-combustion measures (chemical absorption). The budget for phase II was supplied by the ECRA members and industrial project partners such as technology manufacturers and gas suppliers.

The respective research activities within the framework of phase II focussed on investigations regarding solvent regeneration, flue gas characteristics, plant layouts, cost estimations, oxygen supply, process modelling, CO₂ purification and compression. In addition, initial laboratory trials were carried out to investigate the influence of the oxyfuel combustion on the burning process.
5.3 Research Objectives for Phase III

Phase II of the ECRA CCS project comprised detailed investigations on oxyfuel combustion and post-combustion technologies. Accordingly the following work packages for phase III were defined with a focus on oxyfuel and post-combustion technologies:

Work Packages on oxyfuel combustion:

WP A1: “Process Simulation of a Rotary Cement Kiln in Oxyfuel Condition”  
Research Institute of the Cement Industry, Duesseldorf

WP A2: “Burner Design for Oxyfuel Operation of a Rotary Cement Kiln”  
aixergee Process Optimisation, Aachen

WP A3: “Investigation on Clinker and Cement Quality at Oxyfuel Conditions”  
Research Institute of the Cement Industry, Duesseldorf

WP A4: “Optimisation of the Refractory Lining in Oxyfuel Operation of a Rotary Cement Kiln”  
Refratechnik Cement GmbH, Goettingen / Research Institute of the Cement Industry, Duesseldorf

WP A5: “General Layout of a Flue Gas Conditioning Facility for Oxyfuel Operation of a Rotary Cement Kiln”  
Praxair Deutschland GmbH, Duesseldorf

WP A6: “Development of an Overall Concept”  
ECRA Subgroup Oxyfuel

WP A6.1: “Optimised Sealings of a Clinker Production Line for Oxyfuel Conditions”  
aixergee Process Optimization, Aachen

WP A6.2: “Two-stage Cooler Design for Oxyfuel Operation of a Rotary Cement Kiln”  
IKN GmbH, Neustadt

Work Packages on post-combustion technologies:

WP B1: Simulation of amine-based absorption process  
Research Institute of the Cement Industry, Duesseldorf

WP B2: Laboratory experiments on absorbent degradation  
Research Institute of the Cement Industry, Duesseldorf

WP B3: Concept study for pilot trials  
Norcem A/S, Tel-Tek
WP B4: Pre-engineering and design basis for pilot trials
Norcem A/S

The overall project management and coordination was carried out by ECRA (WP C).
Every work package is described in detail in separate reports. This report summarises the major topics and combines the results.
The following main chapters summarise the research activities regarding the oxyfuel work packages (WPs A) and post-combustion work packages (WPs B).
6 Oxyfuel Technology

6.1 General Update

Oxyfuel technology relies on pure oxygen instead of ambient air for combustion. For this purpose the nitrogen is removed in a separation plant (ASU) from the air prior to being supplied to the kiln (see Figure 6–1). Consequently the concentration of carbon dioxide in flue gas is increased significantly. The gas properties are different from those in conventional kiln operation with a corresponding impact on the clinker burning process. 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 flue gas has to be recycled while the recirculation rate adjusts the combustion temperature. Consequently the oxygen concentration becomes an additional degree of freedom, whereas the optimum level must not necessarily be 21 vol %.

![Figure 6–1 Principle of an oxyfuel cement plant](image)

As a consequence of the CO₂-enriched atmosphere in the kiln system (exceeding 80 vol %) only a comparatively simple carbon dioxide purification is required for CO₂ capture. As part of carbon capture and storage technology the purified CO₂ stream is discharged to a compression facility and then delivered to a transport system. Since the final specifications for the CO₂ purity are still being discussed in the scientific community, some uncertainties remain with aspects regarding the overall layout of the CO₂ Processing Unit (CPU).

6.1.1 State of the Art

The technology of oxy-combustion has been applied for example for power generation and in the glass and the steel sector, so far however mainly aiming to increase the efficiency of the burning process. Its application for CO₂-emission reduction has been investigated predomi-
nantly by the energy sector during the past years. Miscellaneous pilot and demonstration fa-
cilities were built and operated (Vattenfall: Schwarze Pumpe, Total, Callide, CIUDEN etc.).
Several demonstration projects are planned (e.g. Jamestown, Youngdong, Jänschwalde)
with a focus on a potential commercial application from 2020 onwards [SCHE, 2011]. Al-
though the test results gained from the energy sector constitute a helpful starting point, the
transferability to the cement industry is limited due to the different requirements in the plant
operation.

Early experiences in the cement industry with the handling of oxygen for combustion were
made especially in the US, the main focus of which was to increase production capacity.
Nowadays trials are carried out aiming at the increase of the substitution rate of low calorific
alternative fuels [LAUX, 2011]. Oxygen enrichment has not been applied to reduce CO₂
emissions in the cement industry so far.

Up to now mainly two different basic scientific approaches have been followed regarding
oxyfuel technology for CCS at cement kilns:

- Full oxyfuel technology applied to the entire flue gases to abate the total CO₂ emissions
  from fuel and material.
- Partial oxyfuel technology applied to the flue gases from the calciner and one preheater
  string. Here the CO₂ atmosphere is enriched in those particular plant aggregates where
  most of the CO₂ emissions are generated. As a result, less plant modifications are nec-
  essary but only up to a maximum of 70% of the total emissions can be captured.

Currently the following projects are reported:

- The Research Institute of the Cement Industry within VDZ has been undertaking a pro-
  ject on the applicability of oxyfuel technology since 2007.
- In ECRA’s phase I the general applicability of different capture technologies like oxyfuel
  was proven in 2007 [ECRA, 2007].
- The International Energy Agency (IEA) published the Technical Study “CO₂ Capture in
  the Cement Industry” in 2008. This basic study deals with the application of oxyfuel
  technology and comprises a cost estimation. A detailed configuration of a partial oxyfuel
  cement plant was considered [IEA, 2008].
- F. Zeman and K. Lackner from the Earth Institute at Columbia University reported in “A
  Reduced Emission Oxygen Kiln” and “Oxygen Combustion in Cement Production” on the
  impacts of oxyfuel combustion on the clinker burning process in 2008/2009 [ZEM, 2009],
  [ZEM, 2008].
- ECRA’s phase II report dealt with the theoretic evaluation of the application of oxyfuel
  technology in cement plants in 2009 [ECRA, 2009].
- The National University of Colombia Granados et. al. studied the numerical simulation of
  oxyfuel combustion in a cement kiln [GRA, 2011].
- In 2011 the Hamburg University of Technology published the first results of their study,
  executed on behalf of Polysius AG. Different layouts of oxyfuel technologies are being
  roughly evaluated concerning energy demand and capture rate [OBE, 2011].

In the meantime patents have been filed concerning the application of partial oxyfuel tech-
nology to a cement kiln. Lafarge (WO 2008/059378 A2) and AirLiquide (WO 2008/056068
A1) referred to the isolation of CO₂-enriched gas produced in the calciner in their patents in

Furthermore, several roadmaps and papers are dealing with economic and social issues of oxyfuel technology as part of CCS. [UNI, 2010; MacD, 2010]

6.1.2 Preconditions for the Oxyfuel Work Packages

The outcome of the ECRA CCS project phase II set the framework for the work packages defined in phase III as follows.

The principal configuration of an oxyfuel cement plant leaves the conventional plant in most parts unchanged and is illustrated in Figure 6–2. In terms of retrofitting an existing kiln plant the initial geometry of the equipment rotary kiln, preheater tower and calciner is kept unchanged. For the reason of gas tightness under oxyfuel operation the sealings have to be optimised compared to conventional operation.

![Configuration of a full oxyfuel cement plant](image)

The grate cooler is fully implemented into in the gas flow, in order to avoid a separate pre-heating of the recycled flue gas and to ensure a high degree of heat recuperation. To prevent CO₂ emissions via the cooler exhaust air/gas the cooler has to be split in two stages. No CO₂ from stage 1 should leak into stage 2. The first cooler stage is operated with recycled flue gas (basically CO₂), which is used in the burning process. As this would result in clinker exit temperatures still too high, a second cooler stage, which is operated with ambient air, is envisaged. This air leaves the cooler as exhaust air and can be used for raw material drying or fuel preparation. A major advantage of using cooler exhaust air for drying purposes is certainly the fact that for example the raw mill must not be operated under air-tight conditions. In
order to increase the drying potential of the cooler exhaust air, additional heat can be recu-
perated from the kiln exhaust gas by the means of a heat displacement system.

Downstream the preheater waste heat is recovered. The efficiency of the recovery units is
limited by the flue gas temperature. The Organic Ranking Cycle (ORC) and KALINA tech-
nologies use organic substances or NH\textsubscript{3} as cycling media, which evaporate at lower tem-
peratures at which steam turbines can not work efficiently. Phase II has indicated that such
systems in conventional operation could generate up to 12 kWh/t of clinker on average. The
remaining flue gas enthalpy is available for raw material drying. As a consequence, the effi-
ciency of the waste heat recovery is more efficient the lower the raw material moisture.

Oxygen from the air separation unit (ASU or the so-called oxidiser) is applied to the burners
in the main firing (as primary "air") and the precalciner. In addition, part of the oxygen is
mixed into the recycled flue gas used as cooling "air" and finally secondary "air". For a me-
dium-size cement plant with a kiln capacity of 3,000 tpd the oxygen demand is estimated to
be around 30 to 35 t/h. Such an amount of oxygen can for logistical reasons only be provided
by an on-site oxygen supply system. Depending on production capacity, oxidiser purity,
separation technology and oxygen pressure, the commercially used air separation processes
require between 0.25 and 1 MWh/t O\textsubscript{2}. Cryogenic oxygen production is currently the most
energy efficient technology for the production of large quantities of oxygen. The economically
optimum purity is between 95 and 97.5 vol %. On this basis phase II has used an oxidiser
purity of 95 vol % O\textsubscript{2}, 3.5 vol % Ar and 1.5 vol % N\textsubscript{2} for the process modelling.

6.2 Full Oxyfuel Technology

The main focus within this project was laid on the application of full oxyfuel technology and
its effects on the burning process as well as its potentials for CO\textsubscript{2} reduction. In order to in-
clude all aspects, partial oxyfuel technology was also investigated on a smaller scale (chap-
ter 6.3).

Interrelation of work packages

The different work packages, as stated in chapter 5.3 interact with each other and corre-
spond to five main aspects: material quality, flue gas, design, operational and retrofitting as-
pects. Material related issues, which are evaluated by experimental investigations, pertain to
product quality (WP A3) and refractory durability (WP A4) aspects. A strong relationship ex-
ists between the optimisation of sealings (WP A6.1) and the flue gas conditioning facility (WP
A5) through the flue gas composition. The development of an oxyfuel burner (WP A2) and
the two-stage clinker cooler (WP A6.2) are topics of the design aspects. As the design also
defines some operational parameters, outcomes of this aspect are included in the process
modelling (WP A1) to execute the operational specifications. To develop a sophisticated
overall layout (WP A6) of an oxyfuel cement kiln including a cost estimation, the identifica-
tion of the retrofitting aspects plays a decisive role. Each aspect is separately evaluated and
summarised.

6.2.1 Product Quality and Refractory Durability Aspects

Oxyfuel operation must ensure that the product quality is not negatively affected. The same
applies to the durability of the refractory lining. Against this background laboratory tests have
been conducted to show the thermo-chemical reaction of both clinker and refractory in a CO₂-enriched atmosphere as in the case of oxyfuel operation.

For both topics similar experimental setups are used. An electrical heated laboratory kiln (Figure 6–3) is utilised, which can provide a maximum temperature of 1,750 °C. Time intervals, temperature gradients and holding time are part of the temperature programs which can be set. Table 6–1 shows exemplarily the temperature program of the clinker burning trials. Two steps were chosen to ensure a complete calcination of the samples at 1,050 °C. During the second step the material is heated up to a maximum of 1,450 °C to simulate realistic conditions in the real kiln.

The burning gas composition is adjusted by means of an upstream gas mixer. The laboratory kiln itself is equipped with a regulator to control the flow rate (see Table 6–2 and Table 6–6).

Table 6–1 Temperature program

<table>
<thead>
<tr>
<th>temperature program</th>
<th>batch</th>
</tr>
</thead>
<tbody>
<tr>
<td>step 1</td>
<td></td>
</tr>
<tr>
<td>gradient 1 [°C/h]</td>
<td>2,100</td>
</tr>
<tr>
<td>temperature 1 [°C]</td>
<td>1,050</td>
</tr>
<tr>
<td>holding time 1 [h]</td>
<td>0.5</td>
</tr>
<tr>
<td>step 2</td>
<td></td>
</tr>
<tr>
<td>gradient 2 [°C/h]</td>
<td>max. (ca. 2,400)</td>
</tr>
<tr>
<td>temperature 2 [°C]</td>
<td>1,450</td>
</tr>
<tr>
<td>holding time 2 [h]</td>
<td>1</td>
</tr>
</tbody>
</table>

Clinker samples in the form of granules are burned in platinum cups. After the holding time the samples are cooled by means of a sieve plate, which is rinsed thoroughly in the desired gas atmosphere until the temperature has dropped to less than 70 °C.

Bricks of the refractory samples are treated directly in the heating chamber without a carrier.

6.2.1.1 Clinker and Cement Quality under Oxyfuel Conditions

In general the chemical and mineralogical reactions of the raw material are affected by several factors like temperature, kiln atmosphere and residence time. Oxyfuel technology significantly influences the kiln operation since the combustion atmosphere has a direct influence
on the temperature profile affecting the clinker phase formation and consequently the product quality.

The impact of a high CO\textsubscript{2} partial pressure on the decarbonation reaction was already investigated in phase II. The experiments have shown an increase of the reaction enthalpy since the decarbonation reaction shifted towards temperatures up to 80 K higher than in conventional operation.

**Experimental setup**

In order to provide a reproducible homogeneity and to eliminate any effect from site-specific raw materials and fuels, all clinkers used for the investigation are produced in the laboratory from standard chemicals as raw materials. A maximum range of clinker reactivity is investigated: lime standard 94–102, silica ratio 1.9–4.7, alumina ratio 0.6–3.4, and degree of sulfatisation 45-130. Five different clinker compositions are chosen. Moreover, C\textsubscript{3}A contents of 0.5 to 9 wt % LOI-free and C\textsubscript{3}S contents of 49 to 75 wt % LOI-free are adjusted.

An experimental matrix of different atmospheres is shown in Table 6–2 covering the conventional conditions as well as different combinations of gas atmospheres for burning and cooling conditions.

**Table 6–2** Experimental set-up of the lab tests on clinker quality

<table>
<thead>
<tr>
<th>Burning atmosphere</th>
<th>Standard</th>
<th>100 vol % CO\textsubscript{2}</th>
<th>75 vol % CO\textsubscript{2}/ 25 vol % O\textsubscript{2}</th>
<th>70 vol % CO\textsubscript{2}/ 30 vol % O\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling atmosphere</td>
<td>Standard</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>100 vol % CO\textsubscript{2}</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>75 vol % CO\textsubscript{2}/ 25 vol % O\textsubscript{2}</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70 vol % CO\textsubscript{2}/ 30 vol % O\textsubscript{2}</td>
<td></td>
<td></td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

**Clinker characterisation**

The chemical compositions of the different clinker confirm a good homogeneity of the synthetically mixed raw material. Furthermore no significant variance of the moduli from the analysed laboratory clinker and the calculated clinker was detected. Moreover, no calcite was detected, thus no recarbonation during the cooling in the CO\textsubscript{2}-rich atmospheres took place. The X-ray diffraction diagrams for the different clinker samples (see Figure 6–4) reveal equivalent clinker phases in standard and oxyfuel samples.
Variations of the alite / belite ratio, which is evidence for the decomposition of alite due to the integration of Fe$^{2+}$ ions into its lattice, are not identified with changing production atmospheres. Likewise the ratio of C$_3$A/ C$_4$AF is almost not affected.

Based on the chemical and mineralogical investigations a few of the clinker samples were selected for the investigation of the microstructure. Figure 6–5 and Figure 6–6 exemplify the microstructure of clinker treated under standard and oxyfuel conditions.

**Figure 6–5** Microstructure of clinker sample burned and cooled under standard condition. Visible on images: Granules, belite cluster, enrichment of basic matrix, details of clinker structure
Figure 6–6  Microstructure of clinker sample burned and cooled under oxyfuel condition. Visible on images: Granules, belite cluster with free lime, enrichment of basic matrix, details of clinker structure

Significant differences between the samples, which can be traced back to the burning or cooling conditions, were not determined. Only two series of clinker showed evidence of more effective cooling in a CO₂-rich atmosphere due to the higher heat capacity of CO₂. The microstructure as seen under the microscope does not reveal an influence of the oxyfuel conditions.

Cement performance

In order to examine the setting behaviour, heat of hydration and strength development of the corresponding cements, the laboratory clinkers are ground under defined conditions to ensure comparability and reproducibility. 3% sulphate agent is added in general in the form of 50/50 hemihydrate and anhydrite to the ground clinkers.

Differential scanning calorimetry (DSC) is used to detect the hydration phases at an early stage (3 h), examples of those measurement results are given in Figure 6–7 for cement pastes from clinker burned and cooled under standard conditions as well as oxyfuel conditions.

Figure 6–7  DSC of cement pastes (3h) based on clinker burned under standard conditions (left) and oxyfuel conditions (right)
The measurements show a comparable composition of the two pastes examined. This is especially the case for the hydration products ettringite, secondary gypsum/hemihydrate and calcium hydroxide (portlandite). No influence of the burning/cooling condition was detected.

Syngenite (K_2Ca(SO_4)_2·H_2O) was detected in standard cement samples and not in the oxyfuel ones. The potassium reacts under oxyfuel conditions with CO_2 to carbonate and instead of reacting with sulphate to syngenite. Based on the absence of syngenite, whose structure contributes to an early setting of the paste, the workability of “oxyfuel cements” is even improved as the early setting is slightly delayed.

The heat of hydration correlates to the reactivity of the cements. Figure 6–8 shows the statistical evaluation of the heat of hydration of all cements tested after 48h, the reference corresponds to the conventional burning and cooling conditions and is set to 100%. The results show a slight tendency towards increased heat of hydration indicating a higher reactivity of the samples produced under oxyfuel conditions. Apparently a CO_2-rich atmosphere influences the setting more than the cooling under oxyfuel conditions. The reason for the faster setting is a marginal increase of C_3A. Correspondingly the content of C_4AF is decreased as it can only form if the iron is present in trivalent form. Thus the higher proportion of aluminium oxide leads to a slight increase of C_3A, which results in a higher reactivity.

![Figure 6–8](image_url) Statistical evaluation of the hydration heat

Mini-prisms made from the different cements are stored under defined conditions and the compressive strength is measured after 2 and 28 days hydration respectively. A visual examination did not show any significant difference in colour of the various prisms. The results are shown in Figure 6–9.
The development of the compressive strength is in line with the development of the heat of hydration which indicates the oxyfuel samples to be marginally more reactive. However, the tendencies are based on small differences in the test results. The samples burnt under conventional conditions but cooled under CO2 atmosphere show a significantly slower strength development: a lower early strength corresponds to a higher 28 day strength as compared to the other samples.

Overall the differences in properties detected for those cements produced under oxyfuel conditions are small and comparable to typical fluctuations in such measurements. The impact of higher CO2-concentration in the kiln atmosphere, on the clinker and the resulting cement properties is negligible.

6.2.1.2 Optimisation of the Refractory Lining in Oxyfuel Operation of a Rotary Cement Kiln

Depending on the kiln zone and the thermal/thermochemical loads, basic or non-basic refractory material is used in the kiln. The durability and suitability of the refractory materials depend on process parameters like temperature level, fluctuation of temperature, chemical attack as well as alternating coating formation.

Phase II of the CCS project had shown the impact of the oxyfuel operation on the kiln atmosphere and the temperature profile in the kiln. The current phase takes a deeper look at brick alteration effects induced by high CO2 gas atmospheres.
**Experimental setup**

Two material types, basic and non-basic material, were investigated concerning their durability. The basic materials exhibit a higher thermal resistance and therefore are suitable for the application in the sintering zone. The characteristics of the three types of basic refractory material are given in Table 6–3.

In the non-basic kiln sections (preheater, calciner, kiln inlet/outlet, cooler), where usually lower temperatures (<1,300°C) prevail, shaped bricks and unshaped concrete refractory materials are used. The characteristics of the three tested non-basic refractory materials are given in Table 6–4.

### Table 6–3 Typical characteristics of the tested basic refractories

<table>
<thead>
<tr>
<th>Basic refractories</th>
<th>Magnesia spinel</th>
<th>Magnesia fused spinel</th>
<th>Magnesia zirconia</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AG 85</td>
<td>AG AF</td>
<td>MG E</td>
</tr>
<tr>
<td>bulk density</td>
<td>2.85–3.00</td>
<td>2.95–3.10</td>
<td>2.90–3.05</td>
</tr>
<tr>
<td>apparent porosity</td>
<td>16–18</td>
<td>13–15</td>
<td>15–17</td>
</tr>
<tr>
<td>MgO</td>
<td>85–89</td>
<td>85–89</td>
<td>92–96</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9–12</td>
<td>9–12</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>–</td>
<td>–</td>
<td>3–5</td>
</tr>
<tr>
<td>CaO</td>
<td>~ 1.0</td>
<td>~ 1.0</td>
<td>~ 1.3</td>
</tr>
<tr>
<td>SiO₂</td>
<td>~ 0.5</td>
<td>~ 0.4</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>~ 0.5</td>
<td>~ 0.5</td>
<td>~ 0.6</td>
</tr>
</tbody>
</table>

Not only the thermal behaviour under oxyfuel conditions, but also the thermo-chemical behaviour in the presence of kiln feed material and material containing volatile compounds (alkalis, sulphur, chlorine), which exhibit a high potential to attack the material, was investigated. For this the refractory test cubes are exposed on one of their surfaces to either an ordinary Portland, a sulphate-resistant cement or a bypass dust to imitate different types of exposure to materials from the process. The initial chemical composition of these materials is shown in Table 6–5.

### Table 6–4 Typical characteristics of the tested non-basic refractories

<table>
<thead>
<tr>
<th>Non-basic refractories</th>
<th>Andalusite-SiC brick</th>
<th>SiC containing concrete</th>
<th>fireclay-zirconia-SiC concrete</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60 AR</td>
<td>50 AR</td>
<td>40 Z AR</td>
</tr>
<tr>
<td>bulk density</td>
<td>2.55–2.70</td>
<td>2.40</td>
<td>2.45</td>
</tr>
<tr>
<td>apparent porosity</td>
<td>13–15</td>
<td>20.0</td>
<td>19.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>46–50</td>
<td>18–22</td>
<td>39–43</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>–</td>
<td>–</td>
<td>3–7</td>
</tr>
<tr>
<td>SiC</td>
<td>13–17</td>
<td>50–54</td>
<td>9–13</td>
</tr>
<tr>
<td>SiO₂</td>
<td>30–34</td>
<td>21–25</td>
<td>35–39</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>~ 1.0</td>
<td>&lt; 0.7</td>
<td>&lt; 1.5</td>
</tr>
</tbody>
</table>

Samples (70 × 70 × 70 mm cubes) of the refractory materials are tested in the electrically heated laboratory furnace under different atmospheric conditions and different thermal/thermo-chemical loads. Due to the restrictions given by the laboratory equipment the exposure time is limited to 8h only. Long term tests are recommended in later phases of the pro-
ject. The temperature level of the basic material and the non-basic material is set to 1,500 °C and 1,200 °C respectively. The different test specifications are given in Table 6–6.

**Table 6–5** Chemical composition of the clinker and bypass dust material which were used for the trials

<table>
<thead>
<tr>
<th>Component</th>
<th>OPC 1)</th>
<th>SRC 2)</th>
<th>BPD 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0.19</td>
<td>0.13</td>
<td>4.21</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.21</td>
<td>0.12</td>
<td>1.01</td>
</tr>
<tr>
<td>LOI</td>
<td>0.40</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>23.44</td>
<td>20.64</td>
<td>9.78</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.02</td>
<td>4.42</td>
<td>2.71</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.19</td>
<td>0.21</td>
<td>0.13</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.06</td>
<td>0.08</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.68</td>
<td>7.54</td>
<td>1.32</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>0.04</td>
<td>0.11</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>1.32</td>
<td>0.79</td>
<td>0.48</td>
</tr>
<tr>
<td>CaO</td>
<td>66.65</td>
<td>64.97</td>
<td>30.85</td>
</tr>
<tr>
<td>Sulphate as SO₃</td>
<td>0.35</td>
<td>0.37</td>
<td>4.24</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.67</td>
<td>0.52</td>
<td>27.28</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.18</td>
<td>0.11</td>
<td>0.55</td>
</tr>
<tr>
<td>Cl</td>
<td>--</td>
<td>--</td>
<td>13.61</td>
</tr>
<tr>
<td>C₃S acc. to Bogue</td>
<td>62.66</td>
<td>66.45</td>
<td>--</td>
</tr>
<tr>
<td>C₃S acc. to Bogue</td>
<td>20.21</td>
<td>9.20</td>
<td>--</td>
</tr>
<tr>
<td>C₃A acc. to Bogue</td>
<td>6.13</td>
<td>0.00</td>
<td>--</td>
</tr>
<tr>
<td>C₄AF acc. to Bogue</td>
<td>8.20</td>
<td>21.11</td>
<td>--</td>
</tr>
<tr>
<td>C₃F acc. to Bogue</td>
<td>0.00</td>
<td>1.06</td>
<td>--</td>
</tr>
</tbody>
</table>

1) OPC = ordinary portland cement, 2) SRC = sulphate resistant cement, 3) BPD = bypass dust

**Table 6–6** Trial conditions under various atmospheric conditions and different thermal/thermo-chemical loads

<table>
<thead>
<tr>
<th>kiln feed material</th>
<th>OPC atmospheric conditions</th>
<th>SRC atmospheric conditions</th>
<th>BPD atmospheric conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxyfuel</td>
<td>Standard</td>
<td>Oxyfuel</td>
</tr>
<tr>
<td>Basic material (1500°C, dwell time: 8h)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AG 85</td>
<td>trial 1</td>
<td>trial 2</td>
<td>trial 3</td>
</tr>
<tr>
<td>AG AF</td>
<td>trial 1</td>
<td>trial 2</td>
<td>trial 3</td>
</tr>
<tr>
<td>MG E</td>
<td>trial 1</td>
<td>trial 2</td>
<td>trial 3</td>
</tr>
<tr>
<td>Non-basic material (1200°C, dwell time: 8h)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>60 AR</td>
<td>trial 7</td>
<td>trial 8</td>
<td>trial 9</td>
</tr>
<tr>
<td>50 AR</td>
<td>trial 7</td>
<td>trial 8</td>
<td>trial 9</td>
</tr>
<tr>
<td>40 Z AR</td>
<td>trial 7</td>
<td>trial 8</td>
<td>trial 9</td>
</tr>
</tbody>
</table>

The following atmosphere specifications are set in the laboratory kiln.

- **Standard atmosphere:** 15 vol % O₂, 10 vol % CO₂, 75 vol % N₂
- **Oxyfuel atmosphere:** 15 vol % O₂, 77 vol % CO₂, 8 vol % N₂
- **Oxyfuel 2 atmosphere:** 3 vol % O₂, 89 vol % CO₂, 8 vol % N₂
The treated refractory samples were finally analysed (X-ray diffraction, chemical analysis, physical properties, microscopy, SEM) to determine the potential wear mechanisms.

**Impact on basic materials**

The macroscopic investigation of the outer surface (Figure 6–10) as well as along structural cuts through the cubes (Figure 6–11) did not reveal a significant infiltration into the basic material under the tested conditions. Even if the hot surfaces which were exposed to the cements and the bypass dust look slightly different, no deep infiltrations or structural transformation are visible at the structural cuts.

![Tested material cubes of AG 85, AG AF, MG E with SCR (standard conditions [top], oxyfuel conditions [bottom])]({})

![Structural cuts of the material cubes AG 85, AG AF, MG E with SCR (standard conditions [top], oxyfuel conditions [bottom])]({})

The impact of oxyfuel operation on basic refractory materials can be discussed taking magnesia spinal (AG 85) material as an example. The magnesia spinel grades exhibit slight clinker melt infiltration at the hot surface including initial contact reactions with the spinel (MA) and the formation of a secondary melt (C\textsubscript{3}MA\textsubscript{2}) (see Figure 6–12).
No significant reaction of the Ordinary Portland Cement (OPC) with the basic brick grades takes place. Sulphate Resistance Cement (SRC) induced some thermo-chemical reaction with the refractory material, however on a low level.
The samples exposed to bypass dust material (BPD) reveal slight salt condensations (sylvine (KCl)) directly beneath the exposed surface, without the salt showing any reaction with the brick material. Clinker, however, also infiltrates the brick material but undergoes a reaction to $\text{C}_3\text{MA}_2$ (see Figure 6–13). The original BPD material contains significant amounts of alkali chlorides and sulphur (see Table 6–5). These components evaporated during the heating process due to their comparatively high partial pressure. Overall the thermo-chemical reactions under BPD exposure are generally more intense compared to the cement exposures, independent of oxyfuel or conventional gas atmospheres.

In summary the basic refractory materials do not show significant differences in wear under the given conventional or oxyfuel atmospheres. In all cases, thermo-chemical reactions with both clinker types (OPC, SRC) and with the BPD material let to a slight infiltration of clinker material into the refractory samples. However, these infiltrations show a dependence on the composition of the bricks and the material they are exposed to. The influence of the “kiln” atmosphere i.e. conventional or oxyfuel conditions seems not to be relevant.

**Impact on non-basic material**

The non-basic bricks and both non-basic concretes reveal thermo-chemical reactions with the cement types resulting in the formation of gehlenite (C$_2$AS) and wollastonite (CS). The bricks exhibited an additional formation of anorthite (CAS$_2$). The mineralogical compositions of the adhering coatings change in all cases under oxyfuel conditions indicating a relevant thermo-chemical reaction. However, the thermo-chemical infiltration is limited to the surface. The structural cuts did not reveal any relevant reaction beneath the surface. (see Figure 6–14 and Figure 6–15).

![Figure 6–14](image)

**Figure 6–14**  Tested material cubes 60 AR, 50 AR, 40 Z AR with BPD (standard conditions [top], oxyfuel conditions [bottom])
When the samples were exposed to BPD intensive thermo-chemical reactions with the non-basic material grades took place independent of the atmospheric conditions. A reaction layer at the hot surface exhibits a glassy phase and significant contents of gehlenite, wollastonite and anorthite. In the case of the two non-basic concretes the formation of glassy phases seems to be slightly more pronounced under oxyfuel conditions.

The formation of a glassy phase mainly depends on the SiC content in the refractory samples as can be seen from sample 50 AR. It contains the highest amount of SiC and exhibits
significant glass formation at the hot surface (see Figure 6–16 and Figure 6–17). The presence of alkalis favours the transformation of SiC to SiO₂ under these temperature conditions resulting in the formation of alkali glass at the hot surface. This underlines the increased thermo-chemical reactions with the various process materials under oxyfuel conditions.

Figure 6–17  Microscopic view of 50 AR exposed to BPD (standard conditions [left], oxyfuel conditions [right])

*Impact on the application area of the materials*

To summarise, basic refractory materials do not exhibit significant differences in wear under the given trial conditions while non-basic refractories reveal certain differences. Therefore the basic materials still seem to be suitable to withstand the requirements in the operational area of the sintering zone under oxyfuel operation. However, the tests reveal an increased thermo-chemical reaction of the non-basic materials. As a consequence the operational area of these bricks in an oxyfuel kiln is limited and the areas with basic lining have to be adapted accordingly.

6.2.1.3  Product Quality and Refractory Durability

In conclusion the laboratory tests do not show any significant impact of the CO₂ atmosphere in the kiln under oxyfuel conditions on the clinker quality. Correspondingly the differences in cement properties are small and under practical conditions not relevant. It should be noted at this point that the tests performed do not cover the effects of different flame characteristics (longer precooling zone, higher CO content) which are outside the scope of these laboratory tests and subject to further research.
The material analysis of the refractories underlined the durability of the basic materials. The refractory lining has to be adjusted with regard to the fact that non-basic materials cannot completely withstand the oxyfuel operation. Moreover the shifting of the calcination reaction to a higher temperature level complicates the application of non-basic materials.

The trials under laboratory conditions were carried out in an electrically heated furnace. Therefore, the lab conditions will not directly reflect practice conditions. Nevertheless, these trials provide a tendency for practical experience regarding refractory wear and cement quality. As the outcomes also depend on the operational specifications, long-term tests are advisable in order to verify this information gained from lab scale tests.

6.2.2 Flue Gas Aspects

The aim of using oxyfuel technology with flue gas recirculation is to produce a flue gas with an adequately high CO₂ concentration, in order to minimise the flue gas cleaning effort. This effort for the energy-intensive flue gas conditioning strongly depends on the composition and the amount of the flue gas. In general the separation of CO₂ from the flue gas is less complex the lower the level of impurities. The composition of the flue gas is defined by the oxidiser purity, the oxygen excess, the composition of fuels and primarily by the degree of false air intrusion. To balance the effort of optimised sealings and the CO₂ purification facility different levels of false air intrusion are specified by the process modelling. 6 % of false air in the flue gas is taken as the reference and the best possible case is based on 2 % of false air respectively.

6.2.2.1 Optimised Sealings

Phase II has shown that the false air intrusion would significantly increase the CO₂ liquefaction costs. As a result the reduction of the intrusion beyond today’s levels by optimising the current sealings becomes even more important for overall energy efficiency.

Phase III focuses on non-permanent joints and on how these should be designed in order to fulfil the requirements of the respective sealing locations most comprehensively. Therefore, sealing locations such as the kiln inlet, kiln outlet, inspection doors, poke-holes, pendulum flap boxes, feed ports and sluices as well as control devices were examined.

Baseline study

To determine the actual ingress of false air through the sealing locations of a clinker production the formula for the Poisseuille flow is used, taking into account the pressure difference between both sides of the sealing, the dimensions and geometrical properties of the sealing gap as well as the temperature and viscosity of the involved gases. The calculation identifies the false air ingress of a conventional clinker production line, operated conventionally and equipped with state-of-the-art sealing technology. Figure 6–18 displays the proportional shares of the several sealing locations of the total false air graphically. The result identifies the kiln inlet sealing, the tertiary air (TA) slide damper, pendulum flap boxes, poke holes and specifically the inspection doors in the upper preheater tower as the major contributors to false air intrusion. These doors by themselves provide approximately one third of the total
false air because of the high differential pressure against which they have to seal. Accordingly, these identified sealing locations provide the biggest potential for false air reduction.

![Figure 6–18](image)

**Figure 6–18** Proportional share in total false air ingress of the several sealing locations

According to the location and nature of the sealing, the prevalent specifics create requirements and side conditions of different importance for each of the sealing locations, which should be taken into account for the development of concepts and designs for improved sealing solutions. **Table 6–7** shows the proposed rating of relevance (++: very relevant → −−: not relevant) depending on the sealing location and its specifics.

To prevent ambient air from entering into the process, three options were looked at, which are presented in general terms as follows:

**Geometrical closure/mechanical design**

The ideal realisation of a mechanically-based sealing is provided by a total geometrical blockage of a potential gap between the two sealing parts. Mechanical design features allow for a complete prevention of false air intrusion only with static sealings or with dynamic sealings if they provide low gap variability (e.g. in case of a shaft sealing with a constant gap width between shaft and bore). In these kinds of dynamic contact sealings, a certain tightening layer will close gaps which are generally necessary for the kinematic function. This tightening layer will be subject to wear and tear. In all other cases of dynamic sealings, gaps will be unavoidable. Another limitation for strict geometrical closure is given by the use of rather rough surfaces, for instance with brick lining, which do not provide the necessary surface closure tightness.
Table 6–7 \hspace{1cm} Characteristics of the sealing locations and their relevance

<table>
<thead>
<tr>
<th>Sealing location</th>
<th>Specifics for sealing locations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>static/ dyn. pairing</td>
</tr>
<tr>
<td>Kiln outlet</td>
<td>++</td>
</tr>
<tr>
<td>Kiln inlet</td>
<td>++</td>
</tr>
<tr>
<td>Inspection doors</td>
<td>−−</td>
</tr>
<tr>
<td>Poke-holes</td>
<td>−−</td>
</tr>
<tr>
<td>Pendulum flap boxes</td>
<td>+</td>
</tr>
<tr>
<td>Feed ports/ sluices</td>
<td>+</td>
</tr>
<tr>
<td>Control devices</td>
<td>−−</td>
</tr>
</tbody>
</table>

Sealgas-flushed / flue gas recirculation

To further reduce the false air intrusion at dynamic sealing locations with unavoidable gaps, the location can be flushed with waste gas. This way, the gas ingress is not air but waste gas from the process itself. To do so, the respective sealing location has to be covered by a suitable hood, which has to be connected to a suitable waste-gas recirculation piping. Unavoidably, there will be new sealing gaps created between the hood and the environment. The challenges of this approach are the safety issues from the leakage of CO₂-containing gases into the working environment. The operation of encapsulated fans might also be critical.

Ambient air suction

Another way to prevent intrusion at dynamic sealing pairs with unavoidable gaps is to provide a lower pressure level at the outside of the sealing compared to its inside. Consequently, there will not be any air intruding into the process, but rather some process gas escaping into the outside. By covering the sealing location with a hood and sucking ambient air from out of the hood, there will always be a small amount of process gas taken out of the process. The suction gas will then preferably be routed towards the air decomposition plant in which oxygen will be produced for the oxyfuel process. Instead of minimizing the intrusion of air into the process, this approach finds its optimum with minimizing the evasion of process gas, which can be achieved by controlling the suitable suction level inside the hoods on the basis of pressure measurements on both sides of the sealing. Wherever no cooling is necessary, the ambient air suction approach might be applicable. The drawback takes the form of higher investment costs and a higher demand on process controls, as the pressure within the suction hoods must be controlled in order to prevent both excessive out-take of process gas and false air intake.
**Design as a combination of three working principles**

The design of a sealing system can of course incorporate more than just one of the working principles shown above. As such, it incorporates shaping, material selections and functionality. Obviously, the creative options are limitless and the objective is to meet the requirements to the maximum possible extent. Due to the fact that these requirements are case-specific, or at least location-specific, the transferability of the sealing systems amongst different sealing locations is limited.

Flow exchange through a sealing is generally best avoided by full contact closure of the gap between the two parts. Strictly, this is only possible with non-dynamic sealing locations. Under acceptance of wear and only minor leakage, such contact sealing types can also be applied in the case of regular, well defined motion patterns of the sealing pairing. The number, orientation and shape of occurring gaps and respective tightening areas (planes or lines) depend on the specific sealing location. In general, a sealing system can more easily be designed if:

- the sealing location has a simple geometry
- the motion pattern of the sealing location is one-dimensional and regular

**Evaluation of sealing solutions**

Based on an analysis of the characterisation of the sealing locations, promising options for the development of the optimised sealings are derived as follows:

- For pendulum flap boxes, small butterfly control valves, poke holes and inspection doors there seems to be no possibility to improve the mechanical or geometrical design. The options to reduce false air ingress are restricted to proper installation and maintenance. The sealing performance may be increased by additional implementation of ambient-air-suction or waste gas flushing technology, however, the multitude of sealing locations and their irregular placement within the preheater tower make both options very complicated.

- Feed ports and sluices need to be operated in a process-inert atmosphere and must therefore be supplied with recirculated waste gas. The last step of the materials’ handling, just before entering into the process, must be operated with dedusted cooled waste gas, and feed chutes must be covered and sealed against the ambient air.

- The efficiency of the kiln inlet and –outlet sealing as well as the tertiary air slide damper can be increased by the application of the flue gas-recirculation technology. Therefore a new design will have to be developed including the necessary process integration. The new design will have to focus on a controlled flow of the coolant (recirculated flue gas) instead of minimised ingress of air (as with conventional systems).

**Table 6–8** displays the technically recommended optimisation paths for the reduction of false air ingress. The displayed potential (++: high potential, ○: low potential, −−: not advisable) does not include an economic cost-to-benefit ratio but shows a mere technical evaluation.

The availability of cooled and dedusted CO₂ rich flue gas at temperatures of around 50°C (after condensation) offers the possibility to utilise the gas for cooling purposes and to generate process-inert atmospheres for material sluices. Especially the solutions for the kiln outlet, kiln inlet and tertiary air slide gate can profit from this waste-gas recirculation approach. For high
temperature sealing locations, this should be sufficient for the provision of appropriate cooling.

Table 6–8   Technical false air reduction potentials for the considered sealing location systems

<table>
<thead>
<tr>
<th>Sealing location</th>
<th>Function principle</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mechanical or geometrical design</td>
<td>Flue gas recirculation</td>
</tr>
<tr>
<td>Kiln outlet</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Kiln inlet</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>TA slide damper</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>TA butterfly valves</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>Poke holes</td>
<td>○</td>
<td>+</td>
</tr>
<tr>
<td>Feed ports/ sluices</td>
<td>○</td>
<td>++</td>
</tr>
<tr>
<td>Inspection doors</td>
<td>○</td>
<td>–</td>
</tr>
<tr>
<td>Pendulum flap boxes</td>
<td>○</td>
<td>–</td>
</tr>
</tbody>
</table>

**Estimation of effectiveness**

In order to judge the possible optimisation options under a techno-commercial aspect, the estimation is outlined as a comparison of four scenarios.

1. **Reference case:** Conventional sealing solution in a realistic state of maintenance after several years of operation

2. **Optimum maintenance:** All sealing locations are equipped with the best possible mechanical design, best practice erection and optimised maintenance (gap width reduction 50%)
3. Improved maintenance: With a more realistic improvement rate (gap width reduction 25%)

4. Waste gas flushed: All optimised sealings and additionally all singularly sealing locations equipped with waste gas-flushed or ambient air suction technologies (kiln inlet, kiln outlet, tertiary air slide damper, feed sluice)

**Figure 6–19** shows the comparison of the discussed scenarios regarding their false air ingress. The reference case displays a total amount of approximately 14% false air related to the total exhaust gas after leaving the preheater. This amount may seem rather high for new plants, but reflects the addition of many small spots of untightness which may occur through the course of time of operation. Irrespective of the absolute figure however, the value serves as a reference for the improvement options covered by the other scenarios.

Scenario 2 “Optimum Maintenance” displays a massive reduction in false air ingress down to approximately only 2%. This is based mainly on the reduction of all sealing gaps down to 50% of their initial height. This could for instance be achieved by frequent replacement of deformed sealing ropes, the application of grease and the replacement of bent metal sheets.

Scenario 3 “Improved Maintenance” also displays a considerable reduction of false air ingress down to approximately 6%. This corresponds to a reduction of all gap heights by 25% (e.g. from 0.5mm down to 0.375mm). This seems to be an achievable scenario.

Scenario 4 “Waste Gas Flushed”: Only 1% of false air enters into the process gas. The main contributors are the inspection doors at high pressure differentials.

**Techno-commercial rating**

Scenario 4 offers the lowest false air intrusion. However, it also requires the highest investment costs, as the seal gas-flushed sealings have to be supplied with the respective gas through long ducts. These costs comprise:

- Costs for ducts and related steelwork
- Costs for hoods around the sealing locations
- Costs for fans and valves
- Costs for instrumentation and control

To provide an adequate flue gas flow for the purpose of waste gas flushed sealings from the extraction point, additional ducts, hoods, supports and fixings are necessary. The required installed steelwork would only lead to an additional investment of €75,000 which would be negligible with respect to the costs for fans, instrumentation and control systems. In total, investment costs of at least €250,000 should be considered for the supply of waste gas to the 4 sealing locations.

The major contributors to false air ingress are inspection doors, poke holes and pendulum flap box covers, mostly those working at high differential pressures. The number of these components and their plant-specific positions do not facilitate the application of seal gas flushed technologies. However, by adherence to high quality design and fabrication of these components, and especially good maintenance, the false air ingress can be kept below 6%. With dedicated efforts in maintenance, false air ingress as low as 3% seems to be achievable without applying waste gas recirculation.
### 6.2.2.2 General Layout of a Flue Gas Conditioning Facility for Oxyfuel Operation

In phase II the influencing factor of the CO\textsubscript{2} purification on the operational costs was identified. Process parameters, which affect the CO\textsubscript{2} purity in the flue gas and the energy demand of the CO\textsubscript{2} Processing Unit (CPU), were also determined.

Based on these findings the CPU was technically designed in phase III and cost estimates improved. The scenarios looked at depend on two factors: the incoming flue gas composition (case 1 - 3) and the final CO\textsubscript{2} purity (case 3 - 4). As the requirements for the final CO\textsubscript{2} purity for transport and storage are still under discussion, two types of CPU designs are evaluated, a partial condensation CPU capable of producing 95.0 vol % CO\textsubscript{2} and a distillation CPU capable of producing 99.9 vol % CO\textsubscript{2}.

**CO\textsubscript{2} purification process**

The CO\textsubscript{2} Processing Unit (CPU) consists of the following sections (see Figure 6–20): flue gas cooling/raw gas compression, activated carbon process for SO\textsubscript{x} /NO\textsubscript{x} removal, dryer, mercury removal, cold box for CO\textsubscript{2} purification, catalytic oxidation reactor, power recovery, and CO\textsubscript{2} product compression. The CPU receives flue gas from the kiln and separates it into (a) pressurized CO\textsubscript{2}, (b) water condensed from the flue gas, (c) acidic waste water, and (d) a stream of non-condensable gas that is vented to the atmosphere.

The CPU is designed to produce CO\textsubscript{2} with a purity exceeding either 95 % or 99.5 % CO\textsubscript{2} suitable for sequestration. The difference in CO\textsubscript{2} purity is achieved using different CO\textsubscript{2} purification cold box designs. For the lower purity a partial condenser is used to separate the CO\textsubscript{2} whilst for the higher purity a distillation column is utilised. In both cases the CPU is designed for a CO\textsubscript{2} recovery of ~ 90 %. Figure 6–20 shows the block flow diagram for the partial condensation system. The diagram for the distillation system differs only in the internal cold box circuitry and is not shown.
Flue Gas Cooling/Raw Gas Compression

After the dust removal and initial cooling of the flue gas from the kiln, part of the flue gas is sent to the CPU and the remainder is used for recirculation. In the CPU, the flue gas is cooled from 50 °C to 27 °C in a water cooled heat exchanger. The CO₂ enters an electrically driven, multi-stage, centrifugal compressor where it is compressed to an intermediate pressure selected for optimal cold box operation. The compression train includes intercooling and after cooling, consisting of water-cooled shell and tube heat exchangers with condensate knockout pots after each compression stage. The presence of moisture in the raw gas compression equipment requires stainless steel construction for all parts to prevent corrosion.

Activated Carbon Process

The activated carbon process is used to remove SO₂ and NOₓ from the compressed raw CO₂. Activated carbon catalytically promotes the oxidation of SO₂ to form SO₃. It also promotes the oxidation of NO to form NO₂. The reaction products, SO₃ and NO₂, are removed with the water when it is drained from the beds as acidic waste water.
**Dryer System**

The raw gas exits the activated carbon process and enters a solid desiccant dryer system, which dries the raw gas to less than 1 ppmv moisture. The system consists of two beds with one bed online while the other bed is being regenerated. The gas stream from the power recovery unit is used to regenerate the offline bed. The regeneration gas is heated before entering the offline bed. After the heating step the bed is cooled using regeneration gas at near ambient temperature.

**Mercury Removal**

To prevent corrosion of the brazed aluminium heat exchanger in the cold box, mercury is removed in an activated carbon bed. Two carbon beds are used in a lead/lag configuration. The carbon is not regenerated on site. Instead, spent carbon is removed and sent to waste disposal or returned to the carbon provider for processing.

**CO₂ Purification – > 95 % Purity**

Purification of the CO₂ takes place in a cold box using a unique process design. The design cools the compressed, dry CO₂ stream using a brazed aluminium heat exchanger (BAHX) down to a temperature at which the majority of the CO₂ condenses. Most of the inerts (oxygen, nitrogen, argon) remain in the vapour phase and are removed using a phase separator. The CO₂ rich (>95% CO₂) liquid stream is then expanded to provide refrigeration to overcome losses and sustain the operation. Both the CO₂ rich stream and the waste inert stream are warmed against the incoming feed stream.

**CO₂ Purification – > 99.5 % Purity**

For the production of gaseous high purity CO₂, a low temperature distillation-based cycle is used. Similarly to the > 95 % purity process, a brazed aluminium heat exchanger (BAHX) is used for heat transfer between multiple streams to make the cold box compact. Refrigeration is provided by expansion of purified CO₂ liquid. The compressed and dried raw CO₂ stream is cooled in a BAHX. It is then passed through the reboiler of the distillation column to provide heat to drive the separation. The CO₂ stream is further cooled, expanded, and then introduced into the top of the distillation column. In the column, the inert gases (oxygen, nitrogen, argon) are concentrated in the top column vapour (vent stream) while the high purity liquid product CO₂ is produced at the bottom of the column. The cold product streams (vent gas and liquid CO₂ product) enter the BAHX and are warmed against the incoming CO₂.

**Catalytic Oxidation**

To minimize carbon monoxide emissions to the atmosphere, vent gas from the cold box is heated and sent to a catalytic oxidation unit (Catox). The catalyst in the Catox unit promotes the reaction of carbon monoxide with oxygen contained in the vent gas to form CO₂.

**Power Recovery**

Power is recovered from the hot vent gas leaving the catalytic oxidation unit by sending it to an expansion turbine. The gas from the turbine outlet is used to regenerate the dryers. The amount of power that can be recovered depends on the rate and pressure of vent gas from the cold box.
**CO₂ Product Compression**

The purified CO₂ stream from the cold box is compressed in a multistage electrically driven centrifugal compressor to the required pipeline pressure. The compression train includes intercooling and after cooling, using water cooled heat exchangers. Because the product CO₂ stream is dry, less expensive carbon steel can be used for the construction of this portion of the compression equipment.

**CPU Performance**

Three different levels of CO₂ concentrations at the inlet of the CPU were evaluated to quantify the effect of air in leakage on the CPU performance. These cases are characterised by the level of air ingress into the kiln as 2 %, 4 % and 6 % air intrusion. To also understand the effect due to different outlet CO₂ purity requirements from the CPU, 95 % and 99.5 % CO₂ outlet concentration were considered for the air ingress of 6 %. These different purity levels require different separation technologies in the CPU.

<table>
<thead>
<tr>
<th>Table 6–9</th>
<th>Performance calculation summary for all cases</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Case No.</strong></td>
<td>1</td>
</tr>
<tr>
<td>Air intrusion</td>
<td>2 %</td>
</tr>
<tr>
<td>Type of CPU</td>
<td>Partial Condensation</td>
</tr>
<tr>
<td>Feed CO₂ purity (dry), mol %</td>
<td>91.5</td>
</tr>
<tr>
<td>Product CO₂ purity, mol %</td>
<td>95.8</td>
</tr>
<tr>
<td>CO₂ capture efficiency, %</td>
<td>93.5</td>
</tr>
<tr>
<td>CO₂ captured, t/d</td>
<td>2,353</td>
</tr>
<tr>
<td>CPU power, kWh/tCO₂</td>
<td>118</td>
</tr>
<tr>
<td>Steam, kg/h</td>
<td>1,796</td>
</tr>
<tr>
<td>Cooling water, m³/h</td>
<td>1,318</td>
</tr>
<tr>
<td>Process water, m³/h</td>
<td>0.78</td>
</tr>
<tr>
<td>Process condensate, m³/h</td>
<td>0.41</td>
</tr>
<tr>
<td>Acid waste, m³/h</td>
<td>0.87</td>
</tr>
</tbody>
</table>

For the partial condensation cases, a process design that works for a wide range of air intrusion rates was selected. Process conditions were chosen to produce CO₂ at a purity of 95 vol % or greater, while minimising average unit power (kWh/tonne contained CO₂). For the distillation case, the strategy was to minimise unit power while producing CO₂ containing 10 ppmv O₂ at a CO₂ capture rate of 90 % or greater. The predicted CPU performance is summarised in Table 6–9.

All gas that enters the CPU exits either as a CO₂ product (sent to underground sequestration), flue gas condensate (sent to waste water treatment), acidic waste water (sent to neutralization) or non-condensables (vented to atmosphere).
The CPU produces two waste water streams. Process condensate contains water condensed from the flue gas as it is cooled and compressed (pH ~ 1.75). Acid waste (pH ~ -0.58) is produced from regenerating the activated carbon beds that are used to remove SO\textsubscript{x} and NO\textsubscript{x} from the compressed raw gas.

The reduction of CO\textsubscript{2}, NO\textsubscript{x} and SO\textsubscript{x} by the CPU is equal to or greater than 99% for each case. Elevated concentrations of contaminate would increase the amount of CPU vent gas. An increase of SO\textsubscript{2} and NO\textsubscript{x} inlet concentration would require larger activated carbon beds for removal and larger quantities of water for the regeneration. As a consequence the acid waste water would increase. Increasing NH\textsubscript{3} concentration in the flue gas may result in a risk of scale formation in the raw gas compression train. The process simulation indicates the risk of scaling to occur at concentrations greater than around 10 ppm of NH\textsubscript{3}.

![Figure 6–21 Layout of the CPU Equipment](image)

Nevertheless, the CPU can handle changes in compositions of non-condensables up to a maximum defined in the design basis for the CPU. For very high maximum inlet concentrations it may be necessary to include additional flue gas treatment upstream of the CPU. If a very high deviation from the design value is of temporary nature, it may be necessary to divert the CPU feed to the conventional stack until the inlet concentration has leveled out. The need for such an action will depend on the extent of deviation from the design value vs. the capacity of CPU to handle the change.

Cost estimation

Figure 6–21 shows a preliminary layout of the CPU with approximate dimensions of 28 x 60m. The largest component is the inlet gas compressor that should be installed in a suitable building. The switchgear and the final CO\textsubscript{2} compressor should also be contained in a building. All process vessels and the cold box can be located in the open.

The following assumptions for utilities were used for the cost estimation of the CPU.

- Currency Conversion € 1.00 = $1.40 US
- Cost of Electricity € 0.071/kWh and € 0.142/kWh
- Cost of Steam € 21.66/tonne
- Cost of Cooling Water € 0.028/tonne
- Cost of Process Water € 0.66/tonne

Table 6–10 shows the capital costs and operating costs associated with the cases as defined in this study. The capital costs estimate quality has a +/−30 % accuracy. Two levels of power costs were added to show the impact of the power cost level on the overall costs.

<table>
<thead>
<tr>
<th>Case No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air intrusion</td>
<td>2 %</td>
<td>4 %</td>
<td>6 %</td>
<td>6 %</td>
</tr>
<tr>
<td>Type of CPU</td>
<td>Partial Condensation</td>
<td>Partial Condensation</td>
<td>Partial Condensation</td>
<td>Distillation</td>
</tr>
<tr>
<td>CPU capital (installed), m €</td>
<td>58.3</td>
<td>58.4</td>
<td>58.5</td>
<td>61.7</td>
</tr>
<tr>
<td>Total unit cost (0.071 €/kWh)</td>
<td>23.90</td>
<td>24.60</td>
<td>25.40</td>
<td>27.20</td>
</tr>
<tr>
<td>Total unit cost (0.142 €/kWh)</td>
<td>32.30</td>
<td>33.20</td>
<td>34.20</td>
<td>36.70</td>
</tr>
</tbody>
</table>

The influence of impurities on energy demand of the CPU is lower than initially assumed. The difference in investment costs using the partial condensation are marginal and the total costs differ only by 6.3 % for a variation of the air ingress between 2 % to 6 %. The influence of the product purity on costs is of the same order. The costs increase by 7.1 % if high purity CO₂ separated by a distillation process is required. For a further increase of the capture rate to 99 % a Variable Pressure Swing Absorption (VPSA) system can be added to the CPU to recover more CO₂ from the vent stream. This method would increase the investment costs but would result in lower specific costs for CO₂ removal due to much higher recovery.

6.2.2.3 Evaluation of Flue Gas Aspects

Basically, the main influencing parameters on the flue gas composition are the degree of false air intrusion, the oxygen purity after air separation and the excess oxygen after combustion. An oxygen excess (fixed at 3 vol %) in the flue gas is essential in order to ensure a complete combustion of fuels. The best oxygen purity was identified as 95 vol % oxygen due to the economics of the air separation unit.

The major contributors to false air ingress are inspection doors, poke holes and pendulum flap box covers. By adhering to high quality of these components and improved maintenance, the false air ingress is expected to be kept below 6 %. With applying waste gas flushed systems at the kiln sealing locations it becomes possible to further decrease the air intrusion to 2 %. Taking into account the relatively modest cost increase in the CO₂-purification and compression unit within the range of 2–6 % false air content, it seems that the use of these flushing systems is not the most recommendable solution. The additional investment costs of approximately € 250,000 and especially the additional operational costs for fans etc. would negatively impact the economics. It is assumed that these costs would exceed the 6.3 % cost increase of the CPU from increasing impurities by false air intrusion.
Instead it is advisable to increase efforts in the design, fabrication and maintenance of conventional sealing technologies to reduce false air ingress down to an achievable 3–5 %. This ingress level will require a review of operational troubleshooting procedures as today inspection doors are unavoidable for operational reasons. As this option has to be limited in the future, a higher reliance on process control systems is necessary. As a basis for further investigations and work packages a realistic target of 6 % with regard to best practice was fixed. In order not to pollute the flue gas, the air guns or shock blowers have to be operated using CO₂ as blowing media. This issue is not discussed in this study.

An even higher influence on cost increase in the CPU than the reduction of false air intrusion is the final CO₂ purity for transport and storage. A requirement of a 99.9 % CO₂ purity will result in a much more complex technology and a corresponding cost increase of 7.3 % as compared to a CO₂ purity of 95 %.

### 6.2.3 Design Aspects

Oxyfuel operation requires major modifications of components compared to existing kiln designs. Most importantly, as identified in phase II, the burner requires an alteration for oxyfuel operation; the cooler also needs to be modified to allow good heat recuperation while CO₂ is recirculated as part of the “combustion air”.

#### 6.2.3.1 Burner Design for Oxyfuel Operation

Phase II has shown that the recycling of CO₂ has an impact on the kiln’s temperature profile. In addition the adjustment of the amount and the concentration of oxygen for combustion allow control of the the energy distribution in the kiln. Based on the numerical process simulation in phase II the impact of oxyfuel operation on the flame formation is simulated by CFD modelling in phase III. A burner design for oxyfuel operation has to take into account both the characteristics of high oxygen concentration as well as CO₂ in the combustion air. An optimum burner operation should prevent damaging effects to the refractory or over-burning of the clinker.

**Method**

Computational fluid dynamics (CFD) is a widely accepted tool for the detailed description of gaseous combustion phenomena and the combustion of particulate coal occurring within a rotary kiln. The CFD model used represents the rotary kiln with the burner and kiln hood to provide proper boundary conditions for the flame region. It contains well-acknowledged and proven standard sub-models for temperature-dependent material properties, turbulence, heat transfer including radiation and conduction within the kiln walls, the Lagrangian multi-phase model to represent the solid fuel kinematics, and heterogeneous and homogeneous fuel reactions. Additional models were developed in this project to describe the main clinker phase reactions in the bed.

The three dimensional computational domain of the freeboard in the kiln is represented by a long tube bounded by the refractory and the surface of the solid bed at the bottom. The burner extends into the kiln on one end of the drum (see Figure 6–22). The refractory itself is explicitly included in the grid in order to simulate heat conduction effects through the stones.
to the ambient and in the refractory along the kiln. Additionally, coating in the sintering zone is considered.

Figure 6–22  Geometry used for modelling

**Generic burner design - Reference**

Various kiln burners for primary fuels are commercially available. However, in order not to prejudice existing burners a generic design was chosen. For this design the following boundaries and/or limitations were considered:

- Upper limit for swirl and axial gas velocity is selected to 250–300 m/s to keep pressure drop in a feasible range
- Lower limit for transport gas velocity is 17 m/s to exclude back draft of the flame
- Inlet temperatures for transport gas is set to 40 °C and for axial and swirl gas to 50 °C due to heating by compressors and by heat transfer through the walls (verified by own measurements in a plant)
- Oxygen level in transport gas for the fuel should not exceed 21 vol % and gas temperature should be kept below 100°C to avoid ignition within the burner channels.

The final design of the generic burner is displayed in Figure 6–23. The objective of this study is the design of a burner which is rather more suitable for oxyfuel application but also appli-
cable to the standard combustion of pulverized coal. The fuel is fed via a central channel, which is surrounded by a swirl gas ring. Both entries are pulled back into the burner with a conical channel in front. This conical part inside the burner is installed in order to enhance the recirculation of the hot combustion product gases. This finally compensates the delayed heating of the gases due to the changes in heat capacities under oxyfuel conditions. Additional air is fed via axial nozzles at the end of the conical opening. This also enhances heating of the transport and swirl gases and offers an additional optimising parameter for oxyfuel operation.

Figure 6–23  Design of the generic burner

The burner is installed parallel to the kiln axis and reaches around 1m into the kiln. The latter is applied to overcome abnormal effects in the fuel particle ballistics due the recirculation zone at the bottom of the kiln at the intersection to the kiln hood.

Based on this geometrical consideration a defined reference case (3000 t/d capacity BAT plant with 3,026 kJ/kg clinker) was adjusted which is identical to the reference of the process modelling.

Impact of oxyfuel operation on flame formation

When switching the reference case to oxyfuel operation by replacing any nitrogen by carbon dioxide, the impact of the CO₂-atmosphere on flame building and clinker formation can be evaluated. Due to changes in the heat capacities of the secondary gas, the cooler exhaust gas temperature will drop.

A “cold” mixture of CO₂ and O₂ has been used as primary “air”. When using recycled gas as primary and transportation “air” it is recommended to reduce the temperature down to near ambient in order to avoid any ignition within the burner channels.
When applying oxyfuel operation to the burner, major phenomena impacting kiln operation become obvious. Comparing the local carbon monoxide concentrations of the oxyfuel base case to the reference case in the near burner region, it can be easily seen that under oxyfuel conditions the CO content is significantly higher, indicating a strong activity of the Boudouard reaction. This finding is underlined if the CO-concentration profile is displayed (see Figure 6–24). Above the sintering zone (first 20–25 m from the burner tip) the average CO-content in the gas is rather doubled if coal is burnt under oxyfuel conditions.

The velocity profile in the near burner region changes significantly due to a volume doubling caused by the Boudouard reaction ($\text{C} + \text{CO}_2 \rightarrow 2 \text{CO}$). This affects the ballistics of the fuel particles and finally stretches the flame further into the kiln. As can be expected, the Boudouard activity strongly affects the temperature profile specifically within the flame. In Figure 6–25 it can be seen that peak temperatures in the flame drop by some hundred degrees due to the endothermic impact of the Boudouard reaction. Since heat transfer from the gas into the kiln is dictated by radiation in the sintering zone, it becomes obvious that finally this effect strongly affects heat transfer from the gas to the material.
The comparative evaluation of the average temperature profiles of both gas and material shows the described effect. Energy is shifted in the gas further into the kiln due to the combustion of the CO produced by the Boudouard reaction and due to lower heat transfer in the sintering zone. This effect forms a longer flame with lower peak temperatures. These phenomena are similar to those observed when lumpy secondary fuels are introduced. Due to the heat shift, material is heated closer to the kiln inlet and the temperature of the bed material exceeds 1,400 °C already at 25 m from the burner tip (see Figure 6–26).

The simulation results have also shown that the Boudouard reaction is the major cause for any change in kiln operation under oxyfuel conditions. At the beginning of phase II of the project, it had been expected that the radiation of the gas changes significantly due to the radiation activity of CO, CO$_2$, and H$_2$O as is observed in power plant technology. Due to the very high dust load in cement kilns the absorptivity/ emissivity of the gas phase is dominated by the particulate matter rather than by the gas. Thus, changes in gas absorption coefficients due to high CO$_2$ content are of a minor extent and negligible.

From the observations and findings described above, it can easily be concluded that clinker formation in the kiln is also affected by oxyfuel operation to some extent. Enhanced activity is the phenomenon which has the most influence on the oxyfuel operation of a cement kiln. It results in:
– Higher gas velocities
– Lower flame temperature and poor heat transfer in the sintering zone
– Heat draft into the transition and sintering zones
– Significant changes in product quality
– Enhanced gasification of the coal particles

Figure 6–26  Flame shape and length – reference vs. oxyfuel base case

Optimisation of the oxyfuel operated burner design

Based on this consideration the burner is adjusted to the oxyfuel conditions by identification of the most suitable data set. The target parameters have been the portions and flows of the 3 primary gas constituents, their velocities and their total portion of the total combustion gas. The final goal is the production of clinker of a sufficient quality. Thus, one should not aim to implement exactly the same flame shape or gas temperature profile. Moreover, the evaluation criterion for oxyfuel burner design is the composition of the clinker.

From the parameter variation strategy it is pointed out, that rising oxygen content in the primary gas tends to be the most efficient measure in terms of producing the same clinker as in the reference case. By combining this with a second measure, namely a higher swirl angle, the kiln state under oxyfuel conditions becomes rather similar to the reference state.

Major changes compared to the reference case are:

1. The volume portion of oxygen in the primary gas (swirl and axial gas) is set to 75 vol %.
   In order to keep overall combustion number of the kiln constant, the oxygen content of the secondary gas is reduced. Thus, no extra oxygen is required.
2. The swirl angle is raised by 10° to 40°.
Both measures are applied to enhance re-oxidisation of the CO produced by the Boudouard reaction and to release the additional heat of the reaction in the flame. This results in a hotter and shorter flame, which is confirmed by the pictures shown in Figure 6–27.

![Image: Local gas temperature on the centre plane – reference vs. oxyfuel optimised](Figure 6–27)

Figure 6–27  Local gas temperature on the centre plane – reference vs. oxyfuel optimised

Figure 6–28 shows the comparison of the gas and clinker temperature profiles in the kiln for the reference case and the oxyfuel optimised case. Both profiles become much more similar. It is expected that besides the adjustment of the burner settings further improvement can be achieved by the adoption of the burner design itself.

Evaluating the phase diagrams of the optimised oxyfuel vs. the reference case, both cases tend to be quite similar except for minor deviations in the clinker formation. From this result it is concluded that deviations in flame building, temperature profile and clinker formation can be overcome by adjustments in the burner settings. From an economic point of view it is concluded that no additional oxygen is required for oxyfuel operation of the kiln. Basically, the operation of a kiln burner under oxyfuel conditions is feasible with the generation of a sintering zone heat profile suitable for the production of clinker.
6.2.3.2 Two-stage Cooler Design for Oxyfuel Operation of a Rotary Cement Kiln

To reduce the overall energy demand for the clinker process it is essential to recuperate as much heat from the clinker as possible. In phase II a two-stage clinker cooler using oxygen-enriched flue gas in the first stage and ambient air in the second was suggested for oxyfuel operation. Replacing ambient air with flue gas as a cooling medium improves the clinker cooling due to the higher specific heat value of the flue gas. In addition CO₂ absorbs radiation better than ambient air, consequently the heat exchange and recuperation rate increases and the clinker is cooled down faster. Overall the cooler efficiency under a CO₂ atmosphere is higher than in conventional operation.

Basically four different cooler types using three different methods are evaluated in phase III. The first concept relies on a continuous clinker bed including either one or two heat shields for separation. The second concept uses an intermediate crusher and the third one is a method which dispenses with movable parts.
Continuous Clinker Bed (CCB) concept

The Continuous Clinker Bed (CCB) concept is based on the proven single stage cooler with heat shield at the neutral point. In this case the focus of the heat shield is the gas separation. Therefore maximal gas tightness with minimal drawback in operation is required.

To fulfil this task two heat shields are considered (see Figure 6–29). The shields are air cooled by forced convection from the top of the cooler and equipped with hardened material at the tip. The gas/air leakage through the gaps between the shield and the cooler walls and roof are minimised by mechanical stops of the refractory at both sides, minimal gaps between the heat shields and the refractory roof and minimal distance between the shield and clinker bed. Maintaining a constant height of the clinker bed becomes mandatory.

![Figure 6–29](image)

**Figure 6–29** Sketch of Continuous Clinker Bed Cooler with two heat shields

Improved seals of the dynamic devices between the flue gas and the ambient air compartments reduce gas/air leakage. The main concern regarding gas/air leakage is the clinker bed itself. Gas and air do not flow through the clinker bed evenly. The air/gas distribution is influenced by the density of the clinker bed, the clinker size distribution and the clinker bed temperature as well as the flow resistance of the clinker bed. In order to reduce the leakage of CO$_2$ from stage 1 to stage 2 through the clinker bed itself, one or more cooling section(s) in front of the first heat shield as well as behind the shield are aerated at a reduced rate.

Between the two shields a zone with reduced aeration is created. The main function of this zone is to act as an air lock. The challenge of this concept is to ensure the right pressure drops before and after the shields in order to avoid air, i.e. in particular N$_2$, leakages to the first stage (see Figure 6–30). Air and gas follow the path of least resistance. In practice this results in flue gas leakage through the clinker bed to the ambient air part of the cooler and ensures that no N$_2$ leaks into the recuperation zone (p$_1$ > p$_2$). Detailed calculations based on gap sizes, pressure differences and gas flow path lines result in CO$_2$ concentration in the cooler exhaust air below 0.5 % at normal operating conditions. The area between the shields
needs to be aerated more strongly than reported earlier. If not, CO$_2$ would escape in larger quantities through the clinker bed itself.

![Diagram of Continuous Clinker Bed Cooler with two heat shields](image)

**Figure 6–30** Pressure distribution of the Continuous Clinker Bed Cooler with two heat shields

The position of the heat shields is fixed by the length of the recuperation zone. The neutral point is maintained directly in front of the first shield. The kiln hood pressure is controlled by the last two fans of the recuperation zone which supplies around 50% of the recuperation gas amount. In the case of a 3,000 tpd production capacity the recuperation zone includes five fans; two for the static grate and three for the movable section. The last two fans of the recuperation zone control the kiln hood pressure and are larger sized than standard to gain flexibility. They are equipped with an inlet vane control and a frequency converter to achieve a wide operation range (0.6–1.2 Nm$^3$/m$^2$s). The additional inlet vane damper is required to compensate for the flat fan curve at reduced fan speed.

The oxyfuel plant is designed to operate with 100% flue gas in the recuperation zone, and this with a range of 75% to 115% of the aerated clinker production capacity. The cooler vent fan is loop controlled to maintain the neutral point directly in front of the first heat shield.

For the passage of large clinker lumps the heat shields need to be opened one after another like an air lock. The system is disturbed and gas leakage (N$_2$/CO$_2$) to the other stage cannot be avoided. The leakage of N$_2$ to the kiln is less than the CO$_2$ which escapes with the cooler exhaust air. The heat shield opens only as wide as is required for the passage of lumps.

Even a cooler design with only one advanced and adapted heat shield seems to be a simpler one and still sufficient for reliable operation. The neutral point must still be maintained in front of the heat shield. A larger amount of flue gas compared to the above concept may escape to the ambient air part of the cooler. The risk of N$_2$ leakage to the recuperation zone at normal operation is still negligible. In order to ensure that flue gas escapes through the clinker bed to the second cooler stage which is operated with ambient air, it might even be useful to reduce the aeration of the rows after the heat shield. For the passage of large clinker lumps
the heat shield needs to be opened. The system is disturbed and \( \text{N}_2/\text{CO}_2 \) escapes to the other stage, which seems to be the biggest concern.

**Intermediate Clinker Bin (ICB) concept**

The second concept envisages a two stage cooler separated by an intermediate crusher, (Intermediate Clinker Bin, ICB). Compared to conventional clinker coolers with intermediate crushers the oxyfuel attempt requires a crusher position far more exposed to the hot zone, i.e. at the end of the recuperation zone (see Figure 6–31).

![Sketch of Intermediate Clinker Bin Cooler](image)

Intermediate crushers are still rarely used and are installed mostly in medium and large size coolers. The crushers are installed after 60–70 % of the total grate area. The advantage of such an installation is that big clinker lumps and coating pieces can be cooled after crushing and the bed height of both cooler sections can be adjusted independently. The drawback of this type of cooler is that under normal conditions, i.e. well granulated clinker, the cooling efficiency is reduced due to the disturbance of the clinker bed, whereas this is partly counteracted by a second clinker distribution zone. Disadvantageously, an additional building height is required (approx 5m) and in the case of an option for a later production increase, the flue gas operated cooler section (stage1) in particular needs to be designed with sufficient grate area reserve. The intermediate crushers available on the market are designed to operate at a higher temperature compared to the back end crushers. Typically, the shafts of the rolls are permanently water cooled.

In the case of the application of oxyfuel technology the crusher has to be positioned at the end of the recuperation zone after approximately 40 % of the grate area. In the case of using
flue gas with only 17–18% oxygen the average clinker temperature is calculated to be between 300 °C and 400 °C. Designing a high temperature resistant crusher by applying special alloys and advanced design, e.g., effective water cooling of the rollers and housing which is suitable for both above mentioned conditions, is possible. Nevertheless, using a similar recuperation gas amount as today results in less thermal stress for the crusher and lowers the risk of this concept.

An arrangement with a chute below the crusher which is less wide than the crusher itself to reduce potential air leakage between both cooler stages has been investigated. To maintain a clinker bed on top of the crusher under all normal operating conditions, the rollers need to be frequency controlled to seal the two stages against each other. Therefore, surface monitoring by a level radar installation or the placement of the whole crusher on load cells is necessary and challenging.

_static separation by the usage of a connection chute_

A third concept is based on the idea “keep it simple” in order to avoid the potential risk of failure of the moveable parts under hot and dusty conditions, which may cause a kiln stop. The installation of a connection chute from the first to second cooler stages without a crusher has been considered. The neutral point is inside the connection chute. As long as the cooling gas fans at the end of the recuperation zone and the cooler vent fan work in conjunction to maintain stable conditions, the neutral point can be maintained inside the chute. Consequently, there is a minimal gas exchange between the two cooler stages. The crusher would be a conventional back end crusher of proven design.

Via CFD analysis it was shown that the separation of both stages can be achieved, but the system would react more sensitively to pressure variation around the neutral point than in the concepts already described. This concept could probably be improved by the installation of a smaller variant of the heat shield in the chute. This shield would reduce the free area between the two cooler stages (connection chute) under normal operating conditions. The size of the chute needs to be designed so that even big clinker lumps and coating pieces can pass to the second cooler stage. Consequently, this chute needs to be bigger than for the ICB cooler installed after the crusher. As an additional feature, injection of flue gas into the chute has been simulated in order to separate the compartments like the gas curtains known from shopping malls. The result is additional mixing by the injected flue gas and the sensitivity to pressure fluctuations remains (see Figure 6–32).
Control systems

Coolers operated with ambient air need control of the bed depth and kiln hood pressure only. The bed depth is controlled indirectly by the compartment pressure of the grate. The kiln hood pressure is loop controlled by the cooler vent air fan. For the newly developed oxyfuel concept this regulation is not sufficient. For the concepts with heat shield(s) the bed depth directly in front of the (first) heat shield has to be monitored closely, e.g. by a level radar to maintain minimal distance between the heat shield and clinker bed to ensure good sealing efficiency between the two cooler stages. For the concept with intermediate crushers the bed depth is not that important, but maintaining a bed on the crusher is mandatory for sealing between the two cooler stages. The bed depth can be controlled by level radar, optical systems or load cells underneath the crusher support. To maintain the neutral point at the specified position is the leading command variable. At the same time the kiln hood pressure has to be maintained within a certain range. This is done by the variation of the last two fans of the recuperation zone. The pressure drops in front and behind the heat shield(s) need to be monitored as part of the control loop. The cooler vent air fan is loop controlled based on the pressure measurement behind the heat shield only. Additional gas analyses (N₂, CO₂) installed in the cooler in front of and behind the heat shield(s) and before and after the intermediate crusher respectively make the system more transparent in order to support the operating team.
Concept Evaluation

Based on the evaluation of the different concepts the cooler using two heat shields was preferably selected for further consideration in this study, mainly with regard to retrofitting and the additional building heights (see Table 6–11). The cooler concept using one heat shield and the connection chute are rejected, as they do not sufficiently match the requirement of gas tightness. Nevertheless, the static cooler concept is developing potential for further investigations.

Table 6–11 Comparison of favourite concepts

<table>
<thead>
<tr>
<th>Issue</th>
<th>Option with 2 heat shields</th>
<th>Option with intermediate crusher</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sealing between stages</td>
<td>Sufficient in normal operation; minor leakage in the case of big lumps</td>
<td>Best possible sealing even in the case of big lumps</td>
</tr>
<tr>
<td>CO₂ in cooler waste air</td>
<td>&lt; 0.5 vol % CO₂</td>
<td>&lt; 0.2 vol % CO₂</td>
</tr>
<tr>
<td>Air leakage in stage 1</td>
<td>Negligible</td>
<td>Negligible</td>
</tr>
<tr>
<td>Potential of cooling big lumps and coating pieces</td>
<td>Limited</td>
<td>Improved due to intermediate crusher</td>
</tr>
<tr>
<td>Cooling efficiency</td>
<td>Optimal</td>
<td>Slightly reduced due to bed disturbance</td>
</tr>
<tr>
<td>Add. building height</td>
<td>+ 0.5 m</td>
<td>+ 5 m</td>
</tr>
<tr>
<td>Grate area</td>
<td>Bigger than standard</td>
<td>Standard</td>
</tr>
<tr>
<td>Risk of concept</td>
<td>Air /gas leakage</td>
<td>Crusher failure</td>
</tr>
<tr>
<td>Cost compared to a standard ambient air cooler</td>
<td>115 %*</td>
<td>115 %* (115-125 %)**</td>
</tr>
</tbody>
</table>

* without civil works, refractory and erection / ** If the recuperation zone is to be designed bigger to provide a reserve for operating with a larger amount of recuperation gas due to process reasons, a reserve for upgrade or additional crusher protection

6.2.3.3 Evaluation of Design Aspects

Two major design aspects, namely the burner and two-stage cooler, which have been identified in phase II, have been conceptually designed. The burner and cooler design in particular rely on each other due to the connecting component of secondary gas. Based on the cooler geometry and performance the secondary gas temperature is determined, whereas the burner characteristics specify the secondary gas composition, like the fraction of recycled gas and oxidiser. Nevertheless these requirements can be aligned with each other.

The concept of the two-stage cooler underlines the technical feasibility of an adequate gas-separation, even in the hot zone of the cooler. Nevertheless, the movable parts in the hot zone bear the risk of more disturbances compared with conventional coolers. In addition the gas-tightness is very sensitive to process fluctuations. In terms of the recirculation rate the presented cooler concepts are limited. The lower the recycled flue gas stream, the smaller
the recuperation area and the hotter the separation device. Retrofitting a cooler seems feasible for recirculation rates exceeding 50%:

The developed burner design cannot be used to retrofit existing burners. Also, the use of alternative fuels requires a specific adaptation, as is the case in conventional burners; a simple adjustment of the flow parameter will not be sufficient since the increased gas velocities will influence the burning characteristics (particles flow). In addition, the oxyfuel burner should allow conventional (air)-operation for e.g. start-ups, shut-downs or failure in the oxygen supply. Typically, the plant is expected to start in conventional operation and to switch to oxyfuel operation once stable conditions are achieved. Switching between both conditions may not impair the process (e.g. temperature) or the clinker quality. It seems that the limiting factor in this respect is certainly the burner. It could very well be the case that an additional, second smaller burner (operated e.g. with oil) could be of help.

6.2.4 Operational Aspects

6.2.4.1 Process Simulation of a Rotary Cement Kiln under Oxyfuel Conditions

In phase II it was shown that the substitution of nitrogen by CO₂ shifts the temperature profile towards the kiln outlet; at the same time the heat transfer changed due to the change in emissivity of the combustion gases. The flow conditions in the preheater are different from those in conventional operation because of the higher density of CO₂, which also affects the gas velocities in the cyclone stages. Finally, the higher specific heat capacity of the recycled flue gas results in an increased capacity stream ratio in the preheater.

Based on the findings in phase II the recirculation rate and correspondingly the oxygen concentration in the combustion “air” are adapted in the model in phase III, the focus of which is on the energetic optimisation by the efficient use of process waste heat, e.g. including raw material drying.

Method: Process modelling

All results from the different work packages in phase II and phase III are combined by an iterative data exchange to be used as input for a process modelling of a full oxyfuel kiln. From this the most relevant process parameters are derived to allow for a well-balanced dimensioning of the various plant components.

The model describes the process from the kiln feed to the discharge of the clinker from the cooler. It comprises individual modules for the plant components such as the preheater, calciner, bypass, rotary kiln and grate cooler. The mathematical calculations themselves cover the energy and material balances for the flows of fuel, dust and gas. The combustion calculations for the fuels, the heat transfer as well as the relevant chemical and mineralogical reactions are taken into account. As results the model provides not only the comprehensive process variables, such as mass and volume flows and their composition, gas and solids temperatures and heat losses, but also the specific energy consumption for burning clinker.

Model enhancement

The existing model is adapted to oxyfuel conditions. The different aggregates for flue gas recirculation are implemented based on the layout in Figure 6-2. A second cooler stage operated with ambient air is added. In addition, the gas-to-gas heat exchanger between the flue
gas and the exhaust air from the second cooler stage is implemented in order to evaluate the direct influence of the raw material moisture on the process operation. Primarily the heat can be recuperated from the flue gas by second cooler stage exhaust air to avoid an air-tight mill. The application of a waste heat recovery unit depends on the residual flue gas enthalpy, as such processes have to be operated continuously. In order to simulate a dry flue gas recirculation a condenser is implemented in the flue gas downstream from the heat exchanger, filter and waste heat recovery unit. This model structure is shown in Figure 6–33.

The air separation unit (ASU) and CO₂ purification unit (CPU) are outside the overall balance boundary.

![Figure 6–33](image-url)  
**Figure 6–33** Full oxyfuel process model structure

**Simulation study**

The results of the oxyfuel operation are compared to a reference case, namely a medium-sized plant with a capacity of 3,000 t/d. Based on BAT consideration for an average energy consumption, the energy demand of the reference kiln in the process model was set to 3,245 kJ/kg clinker.

For oxyfuel operation the following parameters were chosen:

- **Recirculation rate**: The recirculation rate is defined as the ratio of the recycled volume flow related to the overall flue gas volume flow. The oxygen concentration in the combustion “air” is directly influenced by the recirculation rate as a consequence of the mixture ratio of flue gas and oxygen. The total amount of oxygen is determined by the required oxygen for the combustion of fuels, whereas the concentration increases with the decreasing recirculation rate.

- **Humidity of the recirculated flue gas**: In principal the recirculation of dry or wet flue gas is possible; the recirculation of dry flue gas (humidity < 1.5 vol %) requires its drying
through condensation in an additional aggregate providing the appropriate pressure and temperature drop.

- **Waste heat utilisation:** In order not to dilute CO$_2$ in the flue gas flow it cannot be mixed with the cooler exhaust air. Depending on the energy content in the two gas streams and depending where and how much energy is required for drying purposes, heat displacement systems might become necessary.

- **Additional firing:** Depending on the plant specifications - in particular the raw material moisture - an additional firing might become necessary. The most efficient location and the influence on the capture rate were examined.

### Influence of the recirculation rate

A potential retrofit of a kiln with oxyfuel technology allows only marginal geometrical modifications of the existing equipment. Therefore process flows in the model are kept as similar to the conventional plant operation as possible. Taking this as an essential requirement, the model reveals the recirculation rate to be kept in the range of 0.5 and 0.6. The temperature profile in the kiln can still be adapted by the adjustment of the flame characteristics (in work package A2).

A complete new installation offers a higher number of degrees of freedom. Redesigning the plant components, especially adapting the cyclone stage dimensions, allows the recirculation rate and capacity stream ratio (between the kiln feed and enthalpy for preheating) to be further reduced. However, this implies a lower volume flow of recuperation gas and consequently a lower cooler efficiency. At the same time a lower recirculation rate leads to a higher oxygen concentration in the combustion “air” with corresponding higher peak temperatures in the sintering zone result. It is the thermal load in the sintering zone and detrimental effects on material conversion and the refractory that finally prevent the recirculation rate from being reduced to less than 0.5.

The main focus of this study is on the potential retrofit of an existing plant. Thus the recirculation rate ($\sim 0.57$) is determined by an adequate specific recuperation gas amount and the specifications from the burner.

### Influence of the humidity of flue gas recirculation

If the flue gas is not dried before being recycled to the cooler its moisture content can - due to the recirculation - be as high as 12 vol % under the current assumption in the model. Such a “wet flue gas recirculation” requires additional energy demand to heat up the water content, and the cooler efficiency and associated secondary gas temperatures are reduced correspondingly (see Figure 6–34). The temperature profile in the kiln is also negatively affected: despite a higher energy demand the temperature does not increase. The reduced sintering temperature has a negative impact on clinker quality resulting in less alite formation.
Despite the fact that the radiation heat of a gas increases with increasing humidity (see Figure 6–35), the overall effect still results in higher energy consumption. In the current case the model predicts an increase of 2.3% when wet flue gas is recirculated. In addition the risk of corrosion increases due to the condensation of acid gas components in colder parts of the plant. Based on these findings a condenser was implemented into the full oxyfuel model which envisages the humidity in the recirculated gas to be limited to not more than 1 vol %.

Figure 6–35  Emissivity of the flue gas with varying humidity

Waste heat utilisation
Excess heat is available both from the exhaust flue gas downstream from the preheater as well as from the cooler’s second stage exhaust air. While the latter is used for raw material drying the exhaust gas is taken to waste heat recuperation. The ratio between the two heat flows needs to be adjusted by means of a heat exchanger depending on the site-specific situation (raw material moisture, number of preheater stages in existing plants, etc.).
Based on an initial consideration a gas-to-gas heat exchanger was envisaged, the performance of which was simulated in a parameter study. The heat transfer coefficient of a gas-to-gas heat exchanger is restricted to 5 to 35 W/m²K requiring relatively huge heat exchangers for an adequate heat exchange. In addition the capacity-stream-ratio of the gases, which is the driving force for the heat transfer, is also comparatively small in this case. For optimisation reasons different setups of the heat exchanger and additional mixing air ratios were tested.

Heat exchanger variation 1: Ambient air is mixed with the cooler exhaust air before passing the heat exchanger

Heat exchanger variation 2: Ambient air passes the heat exchanger and is subsequently mixed with the cooler exhaust air resulting in higher temperature differences in the heat exchanger.

The characteristics of the gas-to-gas heat exchanger are shown in Figure 6–36. Variation 2 achieves higher recuperation rates and corresponding higher drying capacities due to the increased capacity stream ratio due to the low temperature of the ambient air. Nevertheless only up to 5% of raw material moisture can be dried by the recuperated heat based on the general assumptions (5-stage preheater). However, the flue gas still contains enough energy to operate a continuous waste heat recovery unit after passing the gas-to-gas heat exchanger. For this purpose an Organic Rankine Cycle (ORC) process using pentane as a medium, which can be operated in low temperature range, was implemented into the model.

As the heat transfer coefficient depends on the medium, a heat displacement system was chosen using an oil circuit in order to increase the heat exchange. Two possible concepts were developed; an integrated system and a parallel system (see Figure 6–37). In the integrated system the flue gas heats up the oil, which again warms up the air for the raw material drying. On its way back the residual enthalpy is used for electricity production. In this way the
oil can be recycled to the flue gas heat exchanger with lower energy content. In contrast to this, the parallel system is arranged separately.

Both systems display advantages and disadvantages, but ultimately the parallel system was chosen for further modelling. The decision was based on the higher flexibility of the parallel system, which allows a higher ability to respond to process changes. Thus at lower raw material moisture the efficiency of the first heat exchanger can be reduced by decreasing the air stream and more energy can be supplied to the ORC with less wall losses.

A parameter study shows the dependency of electricity generated against the raw material moisture. Figure 6–38 shows on the left axis the electricity generated in kWh/t of clinker and on the right axis the corresponding additional energy demand given as a percentage of the energy requirement for the ASU and CPU. The less energy required for drying, the more energy is available in the ORC for electricity generation. The blue and gray lines in the diagram refer to 21 vol % oxygen and the different number of cyclone stages respectively. Fewer cyclone stages give a higher energy level in the flue gas and subsequently a higher rate of electricity generation. A higher oxygen level in the combustion gases results in less enthalpy in the exhaust flue gas with correspondingly higher enthalpy in the cooler exhaust air.

Figure 6–37  Heat displacement systems

<table>
<thead>
<tr>
<th>Integrated system</th>
<th>Parallel system</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ More efficient as all streams can be matched to each other</td>
<td>+ Less susceptible to fluctuations of kiln operation</td>
</tr>
<tr>
<td>- Complex system, more sensitive to accident</td>
<td>- Two heat transfer oil circuits</td>
</tr>
<tr>
<td>- Less flexible</td>
<td>+ Independent controlling</td>
</tr>
</tbody>
</table>

The calculations show the strong interdependence of the various parameters which must be adapted to the plant-specific situation. However, some conclusions can be drawn in more
In general terms, based on the boundary conditions given above. Only about 9 kWh/t of clinker can be recovered from the exhaust flue gas which corresponds to 6\% of the additional electrical energy demand for air separation and flue gas conditioning units. Depending on how the process parameters are adjusted and depending on the plant-specific situation a maximum of 6.5\% raw material moisture can be dried without additional firing. In any case the energetic optimisation depends strongly on the given conditions (electricity costs, fuel costs, raw material moisture etc.).

![Graph showing the dependency of produced electricity on raw material moisture and additional energy demand.](image)

**Figure 6–38** Waste heat recovery: Dependency on produced electricity and dried raw material moisture

### Additional firing

Raw material drying solely by process heat is not sufficient at higher moisture rates. Thus for higher values an additional firing is a potential solution to increase the energy level. A disadvantage of installing a combustion chamber is the need to use natural gas as fuel, which is comparatively expensive. Theoretically estimated, additional energy of 200 kJ/kg clinker is necessary to increase the drying capacity from 6 to 8\% material moisture. Firing a typical natural gas composition (85 vol \% methane, \(h_u = 30 \text{ kJ/kg} \)) an amount of approx. 1,200 m\(^3\)/h is necessary to match this increase in energy demand. In principal the hot gas generator (combustion chamber) can be positioned at two possible locations in the plant layout (see Figure 6–39).

In option 1 the hot gas generator is not part of the capture cycle. The CO\(_2\)-containing exhaust gas is released to the environment, corresponding to about 0.007–0.01 kg CO\(_2\)/kg clinker which would decrease the overall capture rate of the kiln by less than 1\%. In option 2 the hot gas is added to the capture cycle itself which requires additional oxygen of about 1.8–1.9 m\(^3\)O\(_2\)/m\(^3\) gas to be added for fuel combustion, since ambient air would not be suitable as combustion air. This configuration allows for the additional CO\(_2\) generated to also be cap-


tured. On the other hand, option 2 requires more energy than option 1 since the heat exchanger efficiency is limited to about 75 to 80%.

![Diagram of combustion chamber](image)

**Figure 6–39** Implementation of a combustion chamber

The flue gas temperature determines the efficiency of the heat recovery processes. Although the ORC is the most efficient system in the given temperature range its efficiency is limited: only 20% of the thermal energy input is converted into electrical energy.

**Energy balance**

**Figure 6–40** shows the main energy streams under full oxyfuel operation. The major part of the overall energy demand, which amounts to 3,245 kJ/kg clinker, is supplied by the fuels, of which 26% finally remain as flue gas enthalpy. This enthalpy is recovered in different steps (HX, WHR, condenser) with a positive impact on overall efficiency. At the same time the temperature of the flue gas is minimised before it is finally cooled down in the CPU.

The second stage cooler exhaust gas corresponds to approx. 10% of the total energy input for raw material drying. This energy content can be further adjusted to the raw material moisture by adjusting the heat exchanger performance.
Integration of findings from phase III

Based on an iterative data exchange between the work packages, deliverables like burner specifications, cooler geometry and degree of false air intrusion were introduced into the process modelling. Likewise new simulation data was transferred back to the respective work package.

Following specifications were implemented:

– Cooler specifications: Continuous Clinker Bed Cooler with two heat shields
  – static grate: 4.4 m², recuperation zone: 26 m², width: 2.8 m, total vented area: 75 m²
– Burner specifications:
  – secondary air: 35,168 Nm³/h (+300 Nm³/h false air at kiln hood), 17.8 vol % oxygen
  – primary air: including swirl, axial and transport gas 2,763 Nm³/h, 62.9 vol % oxygen (of mixture)
– False air intrusion: 6 %
A burner adapted to oxyfuel operation requires a different distribution of the oxygen between primary and secondary gas as compared to conventional burners. While the total amount of oxygen is the same in both cases, oxyfuel operation results in significantly less oxygen in the secondary gas as well as in the tertiary gas. The optimum conditions that still provide sufficient oxygen to the calciner are derived from a parameter study in various steps (scenario 1 to 3). Since the oxygen is only 17.8 % for the optimal burner operation (see chapter 6.2.3.1), the oxygen amount required for fuel combustion in the calciner requires the tertiary gas stream as compared to conventional operation to be increased to 0.68 m$^3$/kg clinker in a first scenario (scenario 1). At the same time the specific cooling gas for the recuperation zone increases significantly to 0.96 m$^3$/kg clinker and the temperature of the secondary and tertiary gas drops correspondingly (compare Table 6–12). Since the temperature of the tertiary gas (<700 °C) ends up being too low for the fuels to be ignited in the calciner, scenario 2 envisages a tertiary gas flow to be reduced to the initial level of 0.58 m$^3$/kg clinker, and oxygen to be injected directly into the calciner via an separate lance.

In the next step (scenario 3) the sum of secondary and tertiary gas is adjusted to the initial value. Thus the tertiary gas flow (0.53 m$^3$/kg clinker) corresponds to a higher secondary gas flow. The total amount of oxygen input is determined by a constant 2–2.5 vol % oxygen content in the flue gas just downstream from the calciner. Under these conditions the temperature in the tertiary gas is 800 °C and the recirculation rate corresponds to 0.57. Table 6–13 shows the resulting flue gas composition at the CPU inlet. Compared to a case of 21 vol % oxygen, scenario 3 results in a slightly lower CO$_2$ concentration in the flue gas. Nevertheless a CPU will be able to handle this gas composition at a similar energy demand as shown above.

In conclusion, scenario 3 has emerged as the optimum one. Its parameters are taken as the basis for work package A6.2 or the iterative data exchange with work package A2.

Table 6–12  Cooler characteristics

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Scenario 1</th>
<th>Scenario 2</th>
<th>Scenario 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen Input</td>
<td>Nm$^3$/h</td>
<td>19,794</td>
<td>17,708</td>
<td>17,009</td>
</tr>
<tr>
<td>Recirculation flow</td>
<td>Nm$^3$/h</td>
<td>100,406</td>
<td>900,392</td>
<td>84,691</td>
</tr>
<tr>
<td>Recirculation rate</td>
<td>-</td>
<td>0.66</td>
<td>0.59</td>
<td>0.57</td>
</tr>
<tr>
<td>Cooling gas</td>
<td>Nm$^3$/h</td>
<td>120,200</td>
<td>108,100</td>
<td>101,700</td>
</tr>
<tr>
<td>Spec. cooling gas</td>
<td>Nm$^3$/kg$_{clinker}$</td>
<td>0.96</td>
<td>0.87</td>
<td>0.81</td>
</tr>
<tr>
<td>Cooling gas temperature</td>
<td>°C</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Secondary gas</td>
<td>Nm$^3$/h</td>
<td>35,171</td>
<td>35,197</td>
<td>35,168</td>
</tr>
<tr>
<td>Spec. secondary gas</td>
<td>Nm$^3$/kg$_{clinker}$</td>
<td>0.28</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>Secondary gas temperature</td>
<td>°C</td>
<td>774</td>
<td>842</td>
<td>879</td>
</tr>
<tr>
<td>Second. gas enthalpy (+dust)</td>
<td>kJ/s</td>
<td>15,114</td>
<td>16,915</td>
<td>17,578</td>
</tr>
<tr>
<td>Tertiary gas</td>
<td>Nm$^3$/h</td>
<td>84,933</td>
<td>72,751</td>
<td>66,430</td>
</tr>
<tr>
<td>Spec. tertiary gas</td>
<td>Nm$^3$/kg$_{clinker}$</td>
<td>0.68</td>
<td>0.58</td>
<td>0.53</td>
</tr>
<tr>
<td>Tertiary gas temperature</td>
<td>°C</td>
<td>700</td>
<td>765</td>
<td>807</td>
</tr>
<tr>
<td>Tert. gas enthalpy (+dust)</td>
<td>kJ/s</td>
<td>32,582</td>
<td>31,366</td>
<td>30,162</td>
</tr>
<tr>
<td>Air cooler cooling air</td>
<td>Nm$^3$/h</td>
<td>100,800</td>
<td>100,800</td>
<td>100,800</td>
</tr>
<tr>
<td>Spec. air cooler cooling air</td>
<td>Nm$^3$/kg$_{clinker}$</td>
<td>0.81</td>
<td>0.81</td>
<td>0.81</td>
</tr>
<tr>
<td>Oxygen enrichment in tert. gas</td>
<td>Nm$^3$/h</td>
<td>-</td>
<td>2,050</td>
<td>2,573</td>
</tr>
<tr>
<td>Spec. energy demand*</td>
<td>kJ/kg$_{clinker}$</td>
<td>3,191</td>
<td>3,118</td>
<td>3,078</td>
</tr>
</tbody>
</table>

* Reference: BAT-level 3,026 kJ/kg$_{clinker}$
Table 6–13  Flue gas condition of scenario 3

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit</th>
<th>Flue gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>wt %</td>
<td>81.8</td>
</tr>
<tr>
<td>N₂</td>
<td>wt %</td>
<td>13.2</td>
</tr>
<tr>
<td>O₂</td>
<td>wt %</td>
<td>2.6</td>
</tr>
<tr>
<td>Ar</td>
<td>wt %</td>
<td>1.2</td>
</tr>
<tr>
<td>H₂O</td>
<td>wt %</td>
<td>1.2</td>
</tr>
<tr>
<td>SO₂</td>
<td>mg/m³ stp</td>
<td>266</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>78</td>
</tr>
</tbody>
</table>

Comparison of the process model and the CFD model

Based on the combined and optimised data from the work packages A1, A2 and A6.2 the process model and the CFD model were compared with respect to their results.

Figure 6–41 and Figure 6–42 show the material conversion in the kiln determined by either model. Compared to conventional operation the flame and burning characteristics change under oxyfuel conditions (lower peak temperatures in the sintering zone, longer precooling zone, energy shifting towards kiln inlet etc.) and the formation of the clinker phases is shifted towards the kiln inlet. Despite these new conditions the models both show that adequate clinker formation takes place even if the raw materials conversion into the clinker phase is slightly different in the two cases. In the process model the aluminium and iron oxide are already converted to intermediate phases (CA and C₂F) at the kiln inlet and the maximum belite content is shifted to the middle of the kiln.

The gas compositions in the kiln inlet as simulated underline the high quality of both models. (see Table 6–14). They provide comparable values although there are slight variations predicted to be in the secondary gas composition. The CFD model shows higher CO₂ concentrations at the kiln inlet, which are consistent with the slightly higher initial secondary gas CO₂ content. In accordance with the lower secondary gas temperatures derived from the burner adaptation the kiln inlet temperature is also higher in the CFD model as compared to the process model.

Table 6–14  Gas composition kiln inlet

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit</th>
<th>CFD model</th>
<th>Process model</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>wt %</td>
<td>82.9</td>
<td>80.7</td>
</tr>
<tr>
<td>N₂</td>
<td>wt %</td>
<td>9.2</td>
<td>9.1</td>
</tr>
<tr>
<td>O₂</td>
<td>wt %</td>
<td>1.7</td>
<td>1.5</td>
</tr>
<tr>
<td>H₂O</td>
<td>wt %</td>
<td>6.2</td>
<td>6.1</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td>1,250</td>
<td>1,136</td>
</tr>
</tbody>
</table>
### Figure 6–41  Material conversion in the kiln (Process model)

![Diagram showing material conversion in the kiln (Process model)]

### Figure 6–42  Material conversion in the kiln (CFD-model)

![Diagram showing material conversion in the kiln (CFD-model)]

#### 6.2.4.2 Evaluation of Operational Aspects

The combination of both the design and flue gas aspects, as well as the operational parameters provides an optimum operational mode for an existing 3,000 t/d cement plant. The results show that a stable operation under oxyfuel conditions is feasible, the oxygen demand being 0.29 t O₂/t clinker and a total CO₂ quantity of ~ 0.84 t CO₂/t clinker being treated by the CPU.
As the plant is operated under slight negative pressure, not much CO₂ can escape from the process. The capture rate is mainly determined by the performance of the CPU. It is independent of the recirculation rate as gas generation and gas discharge are in equilibrium. The total amount of CO₂ generated and captured is however influenced by process parameters such as the fuels used.

Under normal operation the CPU’s capture rate should technically be at least 90 %. This corresponds to 0.76 t CO₂/t clinker to be liquefied for storage. Using an additional technology such as VPSA in the CPU’s vent stream (as explained above) a capture rate of 99 % might be achievable. The leakage of CO₂ from the two-stage clinker cooler (< 0.007 t CO₂/t clinker) is negligible for the overall capture rate. An additional hot gas generator, that might be required in cases of higher raw material moistures, decreases the capture rate by about 1 % for each additional 2 percent-points drying capacity. In summary the capture rate varies between a minimum of 89 % and a maximum of 99 %.

6.2.5 Retrofitting Aspects
The initial theoretical consideration indicated that the application of full oxyfuel technology to an existing clinker burning process would be unlikely. However, the current phase III shows that even for existing kilns a retrofit seem technically feasible. The main findings are summarised in an overall concept as follows.

6.2.5.1 Development of an Overall Concept
Design and operational aspects strongly correspond to each other as illustrated in chapter 6.2.4.1. Simulations indicate a suitable operational mode for retrofit without serious increase in thermal energy consumption. Most parts of the plant can maintain their conventional design. However, the operation of the plant becomes more complex as additional parameters influence the process and extra facilities (ASU, CPU) have to be controlled.

*Interaction of the design and operational mode*

Even if most of the plant design can be kept, the burner and cooler require a more or less completely new design. However, this is not seen as an overall limiting factor to the retrofit. Even different cooler designs can comply with requirements for gas-tightness and adequate cooling performance. The cooler efficiency is even increased due to the gas properties of CO₂, which positively affects process stability by means of sufficient secondary and tertiary gas temperatures.

By adjustment of the burner the flame and burning characteristics can be adapted to oxyfuel operation. Since the temperature profile under oxyfuel conditions is slightly different from conventional operation the choice and location of the refractory in the transition zone also needs to be adapted correspondingly and the area of basic lining expanded. It is of advantage that the new flame characteristics enhance the burnout of fuel particles and provide better protection for the brickwork. Similarly, the risk of unburned fuel falling onto the clinker layer with corresponding negative impact on clinker quality is less under oxyfuel conditions. Due the higher oxygen content the ignition of any type of fuel is improved, which is especially an advantage for the use of many types of alternative fuels. Furthermore, the heat losses
through the exhaust gas are reduced since the total amount of combustion gas is less than under conventional operation.

Sealings can in principle be retrofitted e.g. by waste gas flushed systems if necessary. However, an improved maintenance of inspection doors and similar devices exhibit the highest potential to reduce false air ingress. These measures even seem to be applicable to reduce the false air ingress at older kiln plants. Nevertheless, daily kiln operation requires pokeholes and inspection doors, the use of which can limit the sealing measures significantly. Up to a certain extent the CPU is capable of handling changes in flue gas composition at short-term inspections, which however limit its efficiency.

It is well known that all materials in contact with pure oxygen or liquefied CO₂ are subject to corrosion. But corrosion can also occur under wet flue gas recirculation, as water and acidic components in the flue gas can precipitate at cold points such as where the cold oxygen and hot flue gas are mixed and the temperature level is below the dew point. The integration of a condenser is therefore recommended, even despite higher energy consumption and investment costs.

The achievable capture rate is certainly plant-specific. The biggest impact on the capture rate, as under conventional operation, arises from the raw material moisture. Extremely high moisture content in the limestone might even require an additional firing which reduces the overall capture rate.

Regarding the operation of CPU and ASU most gas producers offer so-called “over-the-fence” solutions. They operate these installations under there own responsibility, but onsite at the cement plant.

**Safety aspects**

Oxyfuel technology comprises certain risks concerning the handling of pure oxygen or leakages of CO₂-enriched gas. Oxygen in higher concentrations significantly lowers the flammability limit of combustible materials. Therefore the oxygen-enriched mixture coming from the ASU must not be used for fuel transport to the burner. Also an accumulation of oxygen in hot areas has to be avoided.

Leakages of CO₂ are possible at the CPU or e.g. waste gas flushing systems. Protective equipment for the employees has to be provided although the CO₂ is not toxic in small concentrations. Emergency shut-downs of e.g. the CPU or the pipeline require a safe release of the gases. For this purpose a stack is required. In existing plants the main stack should be kept.

In general more safety and controlling devices have to be installed under oxyfuel operation and the personnel has to be instructed correspondingly.

**Space limitations**

For the additional aggregates like the CPU, ASU, ORC, auxiliary devices etc. enough space must be available at the plant site. This also applies to any type of additional gas ducts or to a pipeline system for transporting the CO₂ out of the plant.
6.2.5.2 Cost Estimation

For new installations of a complete oxyfuel cement plant an investment cost range between 330 and 360 m€ in 2030 has been reported [CSI, 2009]. Taking a certain learning curve into account after some oxyfuel plants might have been built, the costs range is expected to be reduced to around 270–295 m€ in 2050.

As opposed to a new kiln the retrofit of a cement plant can take advantage of the existing infrastructure. Investment costs for CPU, ASU, auxiliary devices for recycling, sealings, cooler, burner and measurement instrumentation are tentatively estimated to be in the range of 110 to 125 m€ for a 3,000 t/d kiln. This estimate very much depends on the specific plant situation and will certainly be subject to a more detailed study in one of the coming project phases.

Oxyfuel operation will double the specific electrical energy need for cement production in particular due to the energy demand of the CPU and ASU. Figure 6–43 illustrates the operational cost break-down. More than 40% of the operational costs are electricity costs.

![Operational cost break-down](image)

The operational costs have already been reported in detail as an outcome of phase II. Including the costs for CO2 transport and storage as well as the uncertainty of costs for future technologies like oxyfuel the overall CO2-avoiding costs can be estimated in the range of 40 to 60 €/t CO2.

6.2.5.3 Evaluation of Retrofitting Aspects

While at the end of phase II oxyfuel technology only seemed to be applicable to new kilns, the results from phase III show that this technology can also be applied to existing kilns, however not without major investments. It is shown that the CO2 concentration at the stack required for the compression of the flue gases can be achieved in existing kilns, anticipating that the false air intake can be reduced to about 6%. Although this is still a major target under practical conditions, the experts felt that this is achievable with the appropriate maintenance and work behaviour.
However, these results are based on theoretical considerations and need to be both confirmed in further investigations and verified in practical long-term tests at a given time.

6.3 Partial Oxyfuel Technology

6.3.1 Operational and Plant-specific Aspects

The main focus of phase III is on full oxyfuel technology. Nevertheless a comparison of full and partial oxyfuel modes was made by means of the process model. Partial oxyfuel technology was considered as the most likely configuration for retrofitting a cement plant [IEA, 2008]. This statement was based on the assumption that the calciner and one preheater string were operated in oxyfuel conditions and the residual kiln plant in conventional operational mode, thus requiring fewer modifications. The advantage of partial mode is that the CO₂ emissions from the raw material are captured, as well as about 60% of the CO₂ from the fuel combustion.

**Layouts**

**Figure 6–44** Basic layout of partial oxyfuel technology

**Figure 6–44** shows a potential basic layout for the application of partial oxyfuel [IEA, 2008]. The illustrated configuration requires an existing twin preheater tower, wherein one string is included in the recycle stream. The flue gas from this string is split into a recycled and a discharged part. To recuperate the heat from the gas to purification, a heat exchanger is implemented to heat up the oxidiser, which is subsequently mixed to the recycled stream. In order to achieve a comparable energy level of the gas entering the calciner as in conventional operation, the unused tertiary gas transfers energy to the recycle mixture by an additional heat exchanger. **Figure 6–45** provides a more detailed picture of the cyclone constellation of the basic configuration. Both preheater strings consist of four cyclone stages. The combustion gas of the kiln is conveyed to the conventional string on the right side (blue). The oxyfuel string includes the calciner, its cyclone and the preheater string (yellow). The material from both strings is supplied to the calciner and after passing the lowest cyclone enters the kiln. These locations are critical for the gas-tightness against the plant components and their different operational atmospheres.
Basically, the partial configuration provides a high potential for variants. Besides the basic layout another potential configuration is demonstrated in Figure 6–46. While the oxyfuel string uses an existing cyclone preheater, the conventional combustion gas leaving the kiln is used to preheat the recycled flue gas by a gas-to-gas heat exchanger. For this reason the configuration can be an option to retrofit a plant using one preheater string, which however would require a high recirculation rate to keep the preheater functioning. On the other hand a higher capture rate is expected as all CO₂ generated in the preheater is captured.

Figure 6–45  Preheater cyclone constellation

Figure 6–46  Layout variation of partial oxyfuel technology
To increase the thermal energy efficiency the layout envisages additional heat exchangers which increase its complexity. This results in a higher degree of interdependencies between the streams, which makes it more difficult to optimise the operational mode. Small variations of process parameter might have a high influence on thermal energy efficiency.

Both concepts are susceptible to process fluctuations, but the basic configuration (Figure 6-45) offers a higher prospect for maximum energy efficiency compared to the configuration given in (Figure 6-46). Hence this configuration has been examined in more detail:

**Process modelling**

Modelling partial oxyfuel technology the following assumptions have been made:

- plant specification: 3,000 t/d capacity and coal as fuel
- model structure is based on the basic configuration
- oxygen excess was fixed on 3 % in flue gas
- geometry of rotary kiln and grate cooler is fixed due to the request for retrofitting
- only wet recirculation is envisaged as an additional condenser in the recirculation stream would decrease the energy efficiency significantly
- fixed degree of decarbonation of the kiln feed
- no gas leakage at the material transfer from calciner to kiln

The high amount of potential combinations of process parameters result from the structure and the interdependencies. For a maximum overall capture rate, the oxyfuel string should cover as much CO₂ from fuel and decarbonation as possible. In order to find the optimal specification the following parameters have to be taken into account:

- raw meal partitioning to the two preheater strings which influences the capacity stream ratio in preheater strings
- cyclone inlet diameter to regulate gas velocity (optimum 15–20 m/s)
- mass flow of material bypass from preheater string 2 in kiln
- recirculation rate
- oxidiser supply determined by a fixed oxygen excess of 3 %

The simulation study includes two basic scenarios:

- Scenario 1 envisages the redesign of the preheater cyclones in both strings.
- Scenario 2 leaves the preheater cyclones as they are.

**Simulation study - Scenario 1**

Scenario 1 aims at maximum energy efficiency. The geometry of the existing cyclone is iteratively adjusted to the specific gas streams and their properties taking into account the parameter variation given above. The best possible recuperation of heat in the cooler and the optimum temperature profile in the kiln are achieved at a specific secondary gas volume of 0.232 m³_STP/kg clinker. The most efficient recirculation rate is identified to be 0.35. The lower the recirculation rate the lower the energy demand due to the higher temperature level at lower volume flows. However, the preheater and calciner properties limit the further reduction of recirculation as material has to be lifted upstream from the preheater and calciner.

Under these conditions, which provide for efficient and stable operation, 58 % of the total raw material input is fed to the oxyfuel string and no material is envisaged to bypass the calciner.
Based on the selection of parameters the cyclone diameter should be as shown in Table 6–15. Due to the higher CO₂ generation and volume flows in the oxyfuel string, the design of the two preheater strings is different.

Table 6–15  Cyclone inner area (Scenario 1)

<table>
<thead>
<tr>
<th>Cyclone</th>
<th>Initial situation</th>
<th>Oxyfuel string</th>
<th>Conventional string</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.30 m²</td>
<td>4.75 m²</td>
<td>2.60 m²</td>
</tr>
<tr>
<td>2</td>
<td>5.05 m²</td>
<td>5.45 m²</td>
<td>3.00 m²</td>
</tr>
<tr>
<td>3</td>
<td>5.60 m²</td>
<td>5.80 m²</td>
<td>3.50 m²</td>
</tr>
<tr>
<td>4</td>
<td>6.00 m²</td>
<td>6.05 m²</td>
<td>4.05 m²</td>
</tr>
<tr>
<td>5/ Calciner</td>
<td>6.25 m²</td>
<td>6.25 m²</td>
<td>-</td>
</tr>
</tbody>
</table>

The model shows that under partial oxyfuel operation as defined in Scenario 1 the conditions for adequate clinker formation are given. The capture rate strongly correlates with fuel energy efficiency. The requirement of high CO₂ generation in the oxyfuel string limits the possible variables for further optimisation. Taking 90 % capture rate of the CPU as a basis, 70 % of the overall CO₂ generated can be captured. A total of 0.40 m³ stp/kg clinker flue gas with the composition presented in Table 6–16 is ultimately processed in the CPU. This corresponds to 0.607 t CO₂/t clinker of liquefied CO₂.

Table 6–16  Flue gas composition under partial oxyfuel technology (Scenario 1)

<table>
<thead>
<tr>
<th>Component</th>
<th>vol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>76.9</td>
</tr>
<tr>
<td>O₂</td>
<td>3.2</td>
</tr>
<tr>
<td>N₂</td>
<td>7.3</td>
</tr>
<tr>
<td>H₂O</td>
<td>11.4</td>
</tr>
<tr>
<td>Ar</td>
<td>1.14</td>
</tr>
<tr>
<td>SO₂</td>
<td>0.0095</td>
</tr>
<tr>
<td>Cl</td>
<td>0.0006</td>
</tr>
</tbody>
</table>

Due to the separation of the calciner from the kiln the efficiency of the plant decreases and more waste heat from exhaust gases is available. As a consequence the fuel energy demand increases up to 3,536 kJ/kg clinker (+8.4 % compared to conventional operation). The energy flows are shown in Figure 6–47. While being recirculated the energy level of the flue gas needs to be increased in a heat exchanger to achieve a sufficient energy level, comparable to conventional kiln exhaust gases. About 10% of the energy input is provided by the recycled flue gas. From the total energy input to the kiln less than 50% is used for the reactions of the product. Distinctive waste heat is available in the cooler exhaust air and tertiary air, in the exhaust raw gas from the conventional string as well as in the flue gas for the CPU processing. A mixture of tertiary air leaving the heat exchanger and cooler exhaust air would en-
able the drying of raw material with 8% moisture. The CO₂-enriched flue gas stream to the CPU is of only low enthalpy. However, its temperature is still too high for the CPU to work efficiently, but most probably too low to operate a waste heat recovery system continuously. The exhaust from the conventional string could be used for electricity production, however the efficiency might be very low.

![Diagram of energy balance](image)

**Figure 6-47** Energy balance of relevant energy streams using partial oxyfuel technology

**Simulation study - Scenario 2**

In scenario 2 the preheater strings and the cyclone stages are kept unmodified. The simulation takes into account the density and specific heat capacity of the CO₂-enriched gas, which is higher than in conventional operation. This corresponds to a gas velocity of 9 m/s in the cyclone inlet which is too low for stable operation. This can be compensated in the oxyfuel string by adapting the recirculation accordingly. In the conventional string the gas flow needs to be increased, which results in a higher electrical energy demand, and might also require a more powerful exhaust gas fan. The volume of secondary gas rises correspondingly by 68% to 0.39 m³ stp/kg clinker with a subsequent decrease in its temperature. Basically the overall temperature level in the kiln is decreased which requires more fuel input to be compensated. Under these conditions and as compared to scenario 1 the capacity stream ratio in the preheater is increased from 1.4 to 2.2. Thus there is significantly more gas enthalpy available than is needed in the calciner. Since the higher gas volumes in the kiln shift the energy more
towards the kiln inlet, a meal bypass (20% of the kiln feed) was envisaged to keep the kiln inlet temperatures at conventional levels. However, the higher the bypass rate, the higher the risk of coating formation.

Compared to scenario 1 the temperature profile in the kiln in scenario 2 adversely affects the process stability. Figure 6–48 compares the gas and material temperature profile of the optimised (scenario 1, blue lines) and the constant geometry case (scenario 2, green lines) of partial oxyfuel application. Due to the change in the temperature profile clinker formation deteriorates.

![Figure 6–48 Material and gas temperature profile in kiln comparing scenarios 1 and 2](image)

Adjusting the recirculation rate to 0.38, about 0.376 m$^3_{\text{stp}}$/kg clinker flue gas containing 75% CO$_2$ is processed in the CPU. As a combined effect of the higher rate of calcination in the kiln inlet as well as the higher total fuel input, less CO$_2$ is generated in the oxyfuel string and the overall capture rate is decreased to 65% (assuming 90% CPU capture performance).

### 6.3.2 Retrofitting aspects concerning partial oxyfuel technology

Based on the simulation results the ability to retrofit a kiln with partial oxyfuel technology without constraints was evaluated. Although the kiln and cooler remain unmodified, the calciner and preheater have to be adapted. Even if the plant is operated under the assumption of unmodified preheater cyclones (scenario 2), the existing preheater strings have to be gastightly connected for material transfer (compare Figure 6–45). With regard to thermal energy efficiency and the capture rate the retrofitting of an existing twin preheater is regarded as unlikely. In addition, the fans for the two strings have to be adjusted, replaced or in the case of only one existing fan additionally installed.

In any case the calciner requires a redesign, as process parameters cannot be readjusted in order to lift the material using the existing geometry. The riser duct diameter has to be decreased to increase gas velocity to a minimum level.
As for any oxyfuel kiln, false air reduction is crucial in the preheater area and the choice of refractory is important: for partial oxyfuel operation a dedicated focus must be given to air lock systems at the connection of the calciner and kiln inlet. Also, the calcination reaction is shifted towards higher temperatures by higher CO₂ concentration in the combustion gas, which requires an adjustment of the refractory material due to the increased temperature level in the calciner.

Based on these considerations the costs for retrofitting a kiln plant with partial oxyfuel are estimated to amount to 90–110 m € [CSI, 2009].

Operational and safety aspects (control systems) are equivalent to full oxyfuel application (chapter 6.2.5). Similarly, the space requirement for the additional aggregates and the connection to a transport system are equally limiting factors.

### 6.3.3 Partial Oxyfuel Operation in Techno- economical Comparison to Full Oxyfuel Operation

Based on these investigations a comparison of the two techniques (full and partial oxyfuel) has been made taking into account the respective advantages and disadvantages.

Basically both plant layouts allow retrofitting existing kilns for oxyfuel operation. The main focus with full oxyfuel technology is on the redesign of the cooler and the burner, while for partial oxyfuel the preheater and calciner need to be modified. Aspects of false air intrusion, refractory adaptation, impact on product quality, onsite space requirement, safety, as well as operational aspects must be taken into account in both scenarios. Estimated investment costs can be up to 35 m € lower for partial oxyfuel technology, while the capture rate is higher with full oxyfuel design.

![Figure 6–49](image-url)  
**Figure 6–49**  
Electrical energy demand of the different oxyfuel technologies
Operational costs are high in both scenarios due to the thermal and electrical energy demand. The total electrical energy demand of both technologies is shown in Figure 6–49 based on a clinker/cement factor of 0.7. Full oxyfuel design requires more oxygen and in general produces higher volume flows of flue gas than partial oxyfuel operation. The latter has a higher power demand for auxiliary installations due to the complex waste heat utilisation. In total both designs differ from each other in electrical energy per tonne of cement by 10 %, which is still, however, twice as high as under conventional operation.

Correspondingly the CO₂ flows are different in the two scenarios. Figure 6–50 illustrates the CO₂ resulting from the combustion of fuels and the decarbonation of the material. Partial oxyfuel operation is characterised by the direct emissions resulting from the untreated preheater string. Both designs do not capture the indirect emissions from the power generation. Compared to full oxyfuel design the partial oxyfuel operation exhibits lower thermal energy efficiency which results in more waste heat being recovered; consequently the overall directly generated CO₂ flow is higher. At the same time CO₂ leakages are negligible for full oxyfuel operation.

Figure 6–50 Specific CO₂-emissions of the different oxyfuel technologies

Figure 6–51 compares both designs in terms of fuel costs (€/t CO₂ and €/t clinker), thermal/electrical energy demand and captured CO₂ per clinker. The values are specified as differences between the two techniques.
In conclusion, the overall energy consumption of full oxyfuel technology is higher, but direct emissions are lower due to a higher capture rate. As a consequence the fuel and power costs per tonne of cement are correspondingly higher, while the costs per tonne of CO₂ abated are lower compared to partial oxyfuel operation. An overall comparison between the two designs is given in Table 6–17.

Table 6–17  Evaluation of different aspects concerning the full and partial oxyfuel technology

<table>
<thead>
<tr>
<th>Topic</th>
<th>Partial oxyfuel technology</th>
<th>Full oxyfuel technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spec. unabated CO₂ emissions in kg CO₂/kg clinker</td>
<td>0.25–0.35</td>
<td>0.08–0.1</td>
</tr>
<tr>
<td>Capture rate</td>
<td>65–75 % (depending on operational mode)</td>
<td>90–99 % (depending on CPU)</td>
</tr>
<tr>
<td>Retrofitting</td>
<td>feasible with constrains</td>
<td>complex, but feasible</td>
</tr>
<tr>
<td>Electric energy demand</td>
<td>+82 %</td>
<td>+104 %</td>
</tr>
<tr>
<td>(compared to base case, related to t_{cement})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal energy demand</td>
<td>+8 %</td>
<td>+/-0 %</td>
</tr>
<tr>
<td>(compared to base case, related to t_{clinker})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Abatement costs</td>
<td>~ 36 €/t_{CO₂}</td>
<td>~ 33 €/t_{CO₂}</td>
</tr>
<tr>
<td>(30 % released CO₂)</td>
<td></td>
<td>(10 % released CO₂)</td>
</tr>
<tr>
<td>Plant modification</td>
<td>Calciner and preheater</td>
<td>Cooler and burner</td>
</tr>
<tr>
<td>Sealings</td>
<td>high effort necessary</td>
<td>higher effort necessary</td>
</tr>
<tr>
<td>Maintenance</td>
<td>higher effort due to more piping and aggregates</td>
<td>effort mainly resulting from sealings</td>
</tr>
<tr>
<td>Influence on material</td>
<td>high influence on calcination</td>
<td>high influence on calcination, less influence on clinker formation</td>
</tr>
</tbody>
</table>
7 Post-combustion Technologies

7.1 General update

Post-combustion carbon capture technologies are used to remove the CO₂ from the flue gas at the tail end of the clinker burning process. Instead of releasing the CO₂ rich flue gas into the atmosphere, the flue gas is cooled down and the CO₂ is selectively removed from the gas phase (see Figure 7-1). Traditionally, this is done using a liquid CO₂ solvent like an aqueous monoethanolamine solution; upcoming technologies may also use solid sorbents or membranes. In absorption based facilities, the CO₂ rich solvent is transferred from the absorption unit to the desorber unit where the CO₂ is removed from the sorbent [WANG, 2011].

![Figure 7-1](image)

 Principle of a cement plant with post-combustion carbon capture facility

7.1.1 State of the art

While techniques like the amine based CO₂ separation have been employed in industry (i.e. in the oil and gas industries) for decades, first pilot trials in the power sector with post-combustion carbon capture facilities were commenced in 2006. One of the very first pilot plants in the power sector was the amine-based capture facility in Esbjerg, Denmark, which was part of the EC-funded CASTOR-project. Around a dozen other pilot plants have been commissioned since then. The next milestone of commercialisation was achieved early in 2012 when the first large-scale CCS plant went into operation. At the CO₂ Test Centre in Mongstad, Norway, the world’s largest CCS-related post-combustion CO₂ capture facilities were commissioned. Two technologies - the amine absorption process and the chilled ammonia absorption process – are employed to capture CO₂ from a nearby refinery and a gas fired power station.

Techniques using solid sorbents like calcium carbonate are tested on pilot scale. A first project on large scale solid sorbent application was planned in the USA, for the Odessa Cement Plant [CEM, 2010]; the project was discontinued after a concept study due to its high costs.
No further plans for large scale testing with solid sorbent systems are known at the moment. Further upcoming capture technologies such as membranes are still being tested on bench scale.

7.1.2 Findings from ECRA CCS project phase II

Within the previous project phase II, general questions concerning the applicability of post-combustion carbon capture for the cement industry were discussed. It was discovered that cement plants would not be able to supply the capture process with sufficient heat. Compared to power stations where the necessary heat can be supplied at the expense of the plant’s efficiency, there is no sufficient amount of heat available in the cement process. On the one hand the available heat is limited by the actual process efficiency of a cement plant which is usually very high. On the other hand the clinker burning process releases much more CO₂ due to the calcination of the limestone. Related to the total thermal input, the specific CO₂ emission from the cement plant is about five times higher than from a coal fired power station. Cement plants with post-combustion carbon capture therefore need an auxiliary source of heat; it could be either supplied through a nearby plant or by an onsite facility which could be fired by fossil fuels. Alternatively, renewable sources could be used for the heat supply like biomass firing, solar-, or geothermal heating plants.

While upcoming sorbent systems like the chilled ammonia process or the regenerative calcium carbonate cycle seem to be quite insensitive with respect to flue gas impurities, organic amine solvents can be degraded by SO₂, oxygen and other flue gas components. Based on statistical data from German cement plants and literature information on solvent degradation, it has been concluded that about half of the cement plants exceed the acceptable limit on SO₂. If amine scrubbing is used in such plants, additional flue gas desulphurisation will become necessary. Other gas components like nitrogen oxide do not exceed critical limits.

7.2 Simulation of amine-based absorption process

For further investigation and dimensioning of the necessary equipment, a numerical model was built. The model enables the simulation of the thermo-chemical conditions inside the absorption column and the impact of the equipment dimension in correlation with the flue gas parameters like volume flow, temperature and CO₂ concentration.

7.2.1 Mathematical model

The model for the amine-based absorption process is based on the concept published by F.A. Tobiesen et al. [TOB, 2007]. The absorber packing, the relevant part of the column where the absorption process actually takes place, is modelled as a boundary value problem (BVP).

The boundary condition at the gas inlet (packing bottom, $z = 0$) is defined by the chemical composition of the flue gas, its mass flow, temperature and pressure. The opposite boundary condition at the packing top ($z = 1$) is defined by the liquid composition, mass flow and temperature.
The interaction of both streams is defined through differential equations which describe the mass transfer, heat transfer and pressure drop throughout the packing.

Figure 7-2 Sketch illustrating the boundary value problem (BVP) principle. The boundary conditions (BC) are available as start parameters, the heat and mass transfer is described by differential equations.

For the liquid and gaseous stream, the chemical composition and temperature is balanced with the following equations:

\[
-\frac{d\eta_{g,CO_2}}{dz/L} = \frac{L}{\sum n_{g,i}} N_{CO_2} a_i \\
-\frac{d\eta_{l,CO_2}}{dz/L} = \frac{L}{\sum n_{l,i}} N_{CO_2} a_i
\]

In the formula, \(\eta_i\) is the dimensionless molar flow rate and \(N_{CO_2}\) the area-specific molar CO\(_2\) flux between the liquid and gaseous phase which is multiplied with the effective area of the packing \(a_i\). Molar flow and packing length are made dimensionless by multiplying with \(\frac{L}{\sum n_i}\) to achieve the dimensionless molar flow rate as \(\eta = \frac{\dot{n}}{\sum n_i}\) and the dimensionless length as \(\frac{z}{L}\). The same equations are stated for water accordingly.

7.2.2 Technical realisation

The model was implemented using the numerical computational package Scilab [SCI, 2011]. The boundary value problem was solved using the Scilab collocation solver for ordinary differential equations “bvode”. Water and carbon dioxide were considered as transferred components. To simplify the simulation, monoethanolamine (MEA) was considered as a non-transferring component.

The chemical equilibrium was calculated through the equations given by Aboudheir et al. [ABO, 2003]. The mass transfer of CO\(_2\) was estimated through an enhancement-factor model. For the activity of the liquid phase, the electrolyte non-random two liquid model was employed [AUS, 1989]. For the calculation of the heat transfer, the Chilton-Colburn analogy was used [TREL, 1968]. The characteristics of the gas phase were calculated based on the Soave-Redlich-Kwong equation [SOA, 1972].
7.2.3 Verification and results

The modelling results were verified against experimental results reported by Tobiesen et al. [TOB, 2007] (see Figure 7-3). It was found that the simulation results usually are about 15% higher than the experimental results. Obviously the mass transfer model calculated generally too high values for the CO$_2$ absorption rate.

![Figure 7-3](image)

**Figure 7-3** Correlation between simulated and experimental CO$_2$ mass transfer. The simulated mass transfer was found to be approximately 15% higher than the experimental value.

According to the work of Tobiesen et al., the overrated mass transfer usually depends on the enhancement factor function. This enhancement factor is used to describe the mass transfer in the liquid film, where the absorption and solvent reaction actually takes place. Due to the concentration profile that is actually created in the liquid film, the migration of CO$_2$ from the gaseous to the liquid phase is controlled. The concentration profile in the liquid film can be calculated using partial differential equations, this approach is however very time consuming. Therefore, only the enhancement factor model was used for the simulation, accepting that the total deviation is about +/-15%.
The simulations show a high sensitivity against the CO$_2$ concentration. Increased CO$_2$ concentrations in the flue gas promote the capture process; the required absorber height is therefore reduced (see Table 7-1). Minimising the false air in-leakage into the clinker burning process would therefore allow the use of smaller absorber columns and reduces the capital investment. The overall energy demand of the process is rarely affected by the CO$_2$ concentration.

Table 7-1 Simulation results for CO$_2$ absorption with MEA solvent (5-molar) for approximately 90% capture rate and 115 t/h CO$_2$ flow and 40 °C inlet temperature

<table>
<thead>
<tr>
<th>CO$_2$ vol %, dry</th>
<th>Column height m</th>
<th>Column diameter m</th>
<th>Packing volume m$^3$</th>
<th>Capture rate %</th>
<th>Liquid/gas ratio L/m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>23</td>
<td>8.0</td>
<td>1162</td>
<td>89.7</td>
<td>3.9</td>
</tr>
<tr>
<td>18</td>
<td>22</td>
<td>7.1</td>
<td>866</td>
<td>89.3</td>
<td>4.8</td>
</tr>
<tr>
<td>22</td>
<td>21</td>
<td>6.4</td>
<td>676</td>
<td>90.1</td>
<td>5.8</td>
</tr>
<tr>
<td>26</td>
<td>19</td>
<td>5.9</td>
<td>518</td>
<td>90.6</td>
<td>6.9</td>
</tr>
<tr>
<td>30</td>
<td>17</td>
<td>5.5</td>
<td>401</td>
<td>89.8</td>
<td>7.9</td>
</tr>
</tbody>
</table>

7.2.4 Conclusion

The modelling of the monoethanolamine absorption process allowed the dimensioning of the necessary equipment. The results show that the necessary columns do not exceed critical...
limits. The height of these columns is independent of the total throughput, only the cross-sectional area has to be adapted. As the area is a function of the squared diameter, absorption columns with a diameter of about 10 m to 12 m will be sufficient even for the world’s largest cement plants if the CO₂ concentration is not diluted by false air. Increased false air in-leakage will cause larger column diameters accordingly. The calculations have shown the advantage of high CO₂ concentration in several respects. For economic reasons, false air has to be reduced as much as possible to reduce the capital expenses for the carbon capture equipment. A ‘capture ready’ cement plant should have at least a CO₂ concentration of more than 20 % (dry basis) while a concentration above 25 % is preferable.

7.3 Laboratory experiments on absorbent degradation

Well proven CO₂ solvents like monoethanolamine are highly selective and exhibit fast reaction kinetics. However, they also react with other sour gases like SO₂, HCl and HF, forming heat stable salts that are not dissociated in the stripping column. Furthermore, oxygen may react and subsequently degrade the amine solution as well [KOHL, 1997]. Due to the high cost of solvent chemicals and the presence of these amine degrading substances in cement plants’ flue gas, the related reactions between these gases and the CO₂ solvents may cause critical solvent loss and increased operational costs for CO₂ capture facilities.

Acidic gases like SO₂ and HCl react stoichiometrically with amines forming heat stable salts. Heat stable salts are not decomposed in the reboiler, they consequently reduce the amount of amines that take actually part in the CO₂ absorption process. The amines can be recovered to a certain extent in an extra reclamer where soda or potash is added in order to remove the heat stable salts from the amine solution. Nevertheless, for the industrial application of amine scrubbing systems, the limit for SO₂ in the flue gas is usually between 10 ppm and 30 ppm.

Oxygen is another critical substance that may cause amine degradation. The oxygen induced degradation destroys the amine molecule forming several degradation products [SUP, 2001]. The oxygen based degradation mechanism is much less understood, different degradation mechanisms have been discussed in literature, i.e. [PET,1984 and CHI, 2002]. It has been discovered that the oxygen induced amine degradation depends on different parameters like the oxygen concentration, temperature, solvent CO₂ loading and heavy metal ions which could be solved in the amine solution.

To answer the question of how much the cement plants’ flue gas actually affect the stability of amine-based CO₂ solvents, an experimental study was conducted within the project phase III. Its main objectives were the quantification of possible harmful reactions which could degrade the amine solvent, and the estimation of necessary flue gas limits for gases like SO₂ or oxygen.

7.3.1 Experimental set-up

For the laboratory experiment, a synthetic flue gas was mixed from pressurised air, nitrogen and other industrial gases. The premixed gas stream was heated up and saturated with water vapour before entering the reactor. This was important to keep the fluid level in the reactor constant and to prevent it from drying out. In a continuously stirred reactor, the gas was
mixed into 0.5 L of CO₂ solvent (i.e. 5-molar monoethanolamine, MEA) at a flow rate of about 3 litres per minute. The temperature of the reactor was maintained through a thermostat. The vent gas from the reactor was then continuously analysed by infrared spectroscopy in order to measure any volatile degradation products. From time to time, liquid samples were taken out of the reactor and analysed with cationic and anionic chromatography (see Figure 7-5).

**Figure 7-5** Laboratory experiment for the investigation of amine degradation. Gaseous phase is analysed through infrared spectroscopy (FTIR), the liquid phase is analysed through ion chromatography. Particulate matter (PM) and metal salts (Me) can be added to the solvent.

For the field trials, the same reactor was used. As the flue gas from the cement plant had a higher temperature than the reactor vessel, it was cooled down in a moderately heated pipe.

**Figure 7-6** Experimental setup for the field trials.
As the dew point of the flue gas was usually higher than the dew point of the reactor vent gas, the condensation of water vapour would have caused flooding of the reactor vessel. Therefore, condensed water was taken out from the gas stream via a tee connector and a pump (see Figure 7-6).

For the experiments, Monoethanolamine (MEA) was used. It is the most common solvent for CO₂ and is usually applied as an aqueous solution containing 30 wt % MEA.

### 7.3.2 Results

Most results were derived from the FTIR readings as these readings allow the calculation of actual MEA degradation. Figure 7-7 shows an example of three experiments under different conditions. Whenever fresh MEA solution was used, the system initially recorded a huge NH₃ peak due to ammonia that was previously solved in the solution. Once this initial amount of ammonia was released from the liquid, a steady-state ammonia emission was observed due to continuous degradation and subsequent ammonia formation in the liquid.

Oxygen-induced degradation was found to be predominantly dependent on CO₂ loading and solvent contamination. For CO₂ loaded solutions, the measured ammonia emission was usually close to the detection limit. Only CO₂ free solutions showed relevant oxygen-induced degradation. Larger degradation rates were achieved by adding heavy metals like iron and copper salts to the solution (see Figure 7-7). While the metal ions cause significantly higher degradation rates, the CO₂ loading of the solvent again effectively inhibits the degradation reaction.

![Graph showing ammonia concentration over time under different conditions](image-url)

**Figure 7-7** Impact of heavy metal contamination and CO₂ loading on oxygen-induced MEA degradation
The comparison of SO₂ concentration before and after the reactor vessel showed nearly no SO₂ slip through the reactor (see Figure 7-8). Any SO₂ that went to the reactor was completely absorbed in the MEA solution. The measurements show strong correlation between the SO₂ intake and the ammonia output. Especially when the SO₂ concentration in the flue gas is high, the amount of released ammonia is reduced. (See Figure 7-8 and Figure 7-9). This effect is obviously not related to lower degradation but to the high SO₂ intake that reacts with the ammonia and fixes the ammonia as ammonium sulphate in the aqueous solution.

At a cement plant with very low SO₂ concentration (see Figure 7-10), the NH₃ was found to be in the range of the initial flue gas concentration. Because the flue gas in that case contained very little SO₂, no significant fixation of ammonia in the solution was expected.

![Figure 7-8](image.png)

**Figure 7-8** SO₂ concentration at the gas inlet and outlet of the reactor. Usually, the SO₂ reading at the outlet was below the detection limit; measurement from a cement plant with high SO₂ emission.
Figure 7-9  Oxygen concentration in the flue gas and ammonia emission from the reactor at a cement plant with high SO$_2$ emission.

Figure 7-10  Ammonia measurements in the stack and the reactor outlet in a cement plant with very low SO$_2$ emission.
7.3.3 Conclusion

In general, the measured degradation rates were less than expected. Especially CO$_2$ loaded solvents exhibited significantly low degradation rates. Results from literature and experiments show that two general pathways for the degradation of amines exist: sour gases like SO$_2$ and oxygen. Strong sour gases always react with the caustic solvent, a proper gas desulphurisation will be necessary if the SO$_2$ emissions exceed certain limits. Oxygen-induced degradation showed to be much less relevant. Especially the high CO$_2$ concentrations effectively prevent the degradation through oxygen. Small concentrations of iron ions however accelerated the degradation reaction significantly. This underlines the importance of corrosion resistant steel types and the substitution of steel by other materials, if possible. New concepts like the concrete absorption tower with polymer lining which was built for the CO$_2$ Test Centre in Mongstad show suitable solutions in order to reduce the demand of steel and therefore the risk of corrosion and iron contamination of the solvent.

To prevent sour gas-induced degradation, CCS-ready cement plants have to tackle SO$_2$ and HCl/HF emissions if certain limits (10 ppm for SO$_2$) are exceeded. The prevention of oxygen-induced degradation has to be solved by the proper design of the CO$_2$ capture process. Recent projects like the gas suspension absorber which was installed in the Brevik Cement Plant have shown a good SO$_2$ removal rate and a nearly complete removal of HCl and HF.

7.4 Brevik project

Compared to other countries in Europe, Norway has a rather unusual distribution of its CO$_2$ footprint. Unlike many other countries, Norway generates most of its electricity from hydropower; the specific CO$_2$ emission from electricity generation is almost negligible. Most of Norway’s CO$_2$ is emitted through the transportation, industry and petroleum sectors, each of which contributes approximately one fourth to the total CO$_2$ emission. Furthermore, Norway has decided to become carbon neutral by 2030, therefore huge efforts for CO$_2$ mitigation are necessary in all CO$_2$-intensive industries. As a result of this, the preconditions to carry out CCS projects in the Nordic region are good [TEIR, 2010].

Based on a study by the Norwegian Climate and Environmental Agency (KLIF) the Brevik Cement Plant is supposed to be an industrial facility with the lowest cost for CCS in Norwegian industry. In November 2009, the Norwegian government decided to broaden the mandate of the CO$_2$ research and development programme CLIMIT to also include industrial emissions [NOR, 2010].

Based on these unique conditions, the ECRA CCS project group decided to fund and promote the development of a CCS pilot facility in the Brevik Cement Plant. The ECRA project funded a concept study and later co-funded the pre-engineering for the test facility.

The main objective of the Brevik project is to identify the most suitable CO$_2$ capture technology for the cement industry, focussing on post-combustion capture. The project itself was divided into two steps:

- Concept study
- Pre-engineering
The following work packages are subject to the potential next steps:

- Detail engineering
- Construction and operation of the test facility

### 7.4.1 Concept study

Within a first study the general concept for the pilot project was laid down. The fundamental design of the pilot trials defined two parts: On the one hand the ‘test facility’ which would collect a side stream of the cement plant’s flue gas as well as all other necessary utilities. On the other hand, up to three different capture plants could be connected to the test facility and operated simultaneously. A distinct battery limit was defined where the pilot plants would be connected to the test facility. This battery limit also defined the border between the common part of the test facility and the proprietary part for the technology providers.

![Battery limits for the Brevik test facility](image)

**Figure 7-11** Battery limits for the Brevik test facility [NORCEM, 2011]

Based on the design of the battery limits, all input and output streams belong to the interface. Therefore mass and energy balances can be made for each pilot plant without touching the proprietary knowledge inside the pilots.
Overview of the concept study [NOR, 2011]

- Project definition
  - Verify relevant technology suppliers
  - Identify participating technology suppliers
  - Establish agreements with technology suppliers
  - Develop project organisations
  - Grant project financing
  - Agree on technology and equipment ownership
  - Establish overall research programme, parallel or sequential use of the test rigs, etc.
  - Establish project schedule

- Technology verification
  - Verification of the basic process selections
  - Verification of the participating technologies suitable for the test rigs
  - Identification of the utility demand and other requirements for each technology
  - Comparison of the requirements from the suppliers with the possibilities at Norcem
  - Specification of the utilities existing at Norcem today
  - Design (size and type) of the required utilities

- Research programme
- Concept Study report

7.4.2 Pre-engineering

The scope of work in this project has been to establish the necessary decision basis for technology requirements and costs regarding the installation and operation of a test centre at Norcem Brevik. In order to qualify one or more capture technologies for the optimal removal of CO₂ from the cement flue gas system, a test program has been developed in co-operation with the technology providers. The full report of a corresponding pre-engineering study was worked out by Norcem for internal use [NOR, 2011].

Based on input from the technology providers, necessary modifications and new installations required for facilitating the CO₂ test site activities were specified. The test centre is designed for three technologies testing in parallel in addition to at least one at the time upcoming small scale technology. The test center will have a lifetime of 3 to 5 years and equipment and materials are selected from this perspective. A test period of 6 months is envisaged for each technology. For available mobile CCS test units necessary modifications were indentified. For technologies where no mobile test units exist so for, a design basis was proposed. Related costs for detail engineering, manufacturing and pilot operations in Brevik were specified.

The key findings are as follows:

- three CCS techniques were selected for the first trials
- the cement plants flue gas was characterised with respect to the pilot plant requirements
- available space in the cement plant and all necessary supplies (water, energy etc.) were defined
- an accompanying research program for the pilot trials was developed
deliveries for each pilot trial

a preliminary cost estimation for the construction and operation of the test facilities

Tel-Tek (Telemark Research Institute) has supported the project with technical assistance on CCS in addition to being responsible for the development of the research program. This report summarises the work and findings revealed in the Concept Study and Pre-engineering of the small scale CO₂ capture test facility at Norcem’s cement plant in Brevik. Recommendations for further work and preparations for the next phase are suggested.

7.4.2.1 Flue gas characteristics

As a design basis for the pilot plant, a general survey of cement plants' flue gases was prepared. Based on available emission data all cement plants in Germany and some other European cement plants were included in the survey. This plant group is unlikely to be representative for the complete cement sector. Nevertheless, it represents a large number of plants with extensive and state-of-the-art flue gas cleaning systems. Due to this fact, the data was considered as reasonable for compiling a general flue gas description with respect to the application of post-combustion carbon capture in the cement industry.

For the description of the flue gas, yearly averages of NOₓ, SO₂ and particulate matter emissions were collected. To describe possible fluctuations due to the process and the impact of certain flue gas cleaning systems, readings from the continuous emission measurement system from the Brevik plant were also evaluated.

7.4.2.2 Flue gas tie-in and monitoring

To allow a wide variation of the flue gas quality, two flue gas tie-ins are planned for the test facility. The primary tie-in is intended to be after the last flue gas cleaning step, the bag-house. A secondary tie-in would be installed after the evaporative cooler to bypass the flue gas cleaning (deSOₓ and dedusting). By mixing those streams, different levels of flue gas impurities like particulate matter, sulphur dioxide and HCl can be achieved. Although the deNOₓ facility cannot be bypassed, the plant’s permit allows reducing the deNOₓ for testing purposes, therefore the NOₓ concentration can be changed as well.

Figure 7-12 Flue gas tie in and monitoring points
According to the battery limit concept, all input and output streams will be monitored with respect to the gas composition, energy and cooling water consumption. The monitoring is carried out simultaneously where possible. Other measurement points are alternately monitored like the continuous gas analysis. A high sampling frequency and continuous draft on all gas probes allow a sufficient data quality in this case.

7.4.3 Selected CCS techniques

Three different techniques were selected for the first trial phase of the pilot facility. They were selected based on the availability of piloting equipment and technical diversity. The techniques selected for the initial testing stage are:

– Amine scrubbing (Aker Clean Carbon)
– Chilled ammonia process (ALSTOM)
– Regenerative carbonate cycle (ALSTOM)

These three techniques offer a wide variety of fundamental capture principles, operating conditions, possible degradation reaction and final CO₂ purity. While many more capture systems exist already, they offer more or less the full spectrum of capture technologies which should be available for carbon capture in the mid-term.

Table 7-2

<table>
<thead>
<tr>
<th>liquid phase</th>
<th>solid phase</th>
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<tbody>
<tr>
<td>organic</td>
<td>amine process</td>
</tr>
<tr>
<td>inorganic</td>
<td>chilled ammonia</td>
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7.4.3.1 Amine scrubbing

The Advanced Amine Process from Aker Clean Carbon is based on the classical amine scrubbing process for CO₂ which was developed in the 1930’s. A CO₂-selective organic solvent is circulated between two packed columns. In the first column, the absorption takes place, the second column is used to separate the CO₂ from the solvent. As amine scrubbing technology is well proven in the petroleum sector and therefore commercially available, it might be one of the technologies that could become relevant for the commercial application of CCS in the power sector and the cement industry.

The amines used for the capture process are usually low-volatile and highly selective. Due to the highly selective transfer of CO₂ from gas to liquid phase, CO₂ is captured at very high purity, usually greater than 99.9 %. In the desorption process, the solvent is heated up using low pressurised steam. This part of the process has a high energy demand. Depending on the actual conditions; the amine scrubbing requires between 2800 kJ and 3500 kJ per kg of captured CO₂.
The reactivity of the solvent chemical also has disadvantageous effects. In particular, oxygen and sour gases like SO₂ can react irreversibly with the solvent. The reaction with sulphur oxides is very fast and the complete amount of SO₂ reacts with the solvent chemical. For plants with increased SO₂ levels in the flue gas, additional waste gas pre-treatment will be necessary.

7.4.3.2 Chilled ammonia

Aqueous ammonia is another relevant solvent for CO₂ capture. While ammonia is similarly suitable to react with CO₂, it is far cheaper than amine-based solvents. Potential solvent losses due to degradation will therefore cost much less. Due to its low chemical complexity, the formation of toxic or corrosive degradation products is much less problematic. On the contrary, ammonia is very volatile. The volatility requires a lower temperature regime in the absorber section (about 10 °C) and an additional washing section at the top of the absorber. Furthermore, the bound CO₂ precipitates as ammonium bicarbonate. The handling of this suspension requires more sophisticated equipment compared to the amine process.

The Chilled Ammonia Process is one of the two capture techniques being demonstrated at the CO₂ Technology Centre Mongstad (Norway).

7.4.3.3 Carbonate looping

A relatively new and upcoming carbon capture process is the carbonate looping process, also known as the regenerative carbonate cycle. Unlike the amine and ammonia processes, a dry limestone-based absorbent is used to capture CO₂. The process consists of two fluidised bed reactors, the carbonator and the calciner. In the carbonator, the CO₂ reacts with the limestone within a temperature range between 600 °C and 700 °C. The CO₂ is then subsequently removed from the limestone in the calciner at 900 °C. After each fluidised bed, the solid phase is separated from the gas stream and fed to the opposite reactor vessel.

The calciner has to be operated under oxyfuel conditions to prevent the dilution of the captured CO₂ with nitrogen; the oxygen demand is about 40 % in relation to the oxygen demand of an oxyfuel kiln.

A major advantage of the regenerative carbonate cycle is the absorbent. Instead of expensive or corrosive chemicals, the process uses finely ground limestone. As limestone is usually available in the vicinity of a cement plant, the plant could supply itself with the necessary CO₂ absorbent. Although the limestone delivers a fairly cheap material for CO₂ absorption, it has to be replaced after a certain number of capture cycles. The consumption of absorber material is therefore much higher compared to solvent-based capture facilities. However, the used and degraded limestone from the carbon capture unit can be fed directly into the cement clinker production process avoiding any waste stream from the capture process.

For the Brevik Project, it was investigated whether the limestone fines for the carbonate looping process could be supplied through the plant’s limestone quarry and its grinding facilities. While the limestone quality from the quarry was considered to be suitable, it emerged that it would be difficult to achieve the particle size distribution required for the carbonate cycle.
8 Summary

Within the ECRA CCS Project Phase III two major CCS technologies were investigated with respect to their application in the cement industry, namely the amine-based post-combustion carbon capture and the oxyfuel combustion process. Several work packages were defined and assigned to external project partners who carried out the related research work. The possible impact on the cement production process was evaluated as well as questions concerning the CO₂ processing, plant integration and energy efficiency.

Oxyfuel Technology

Oxyfuel technology involves the combustion of fuels with pure oxygen in combination with the recycling of flue gas to moderate the temperature profile. As a consequence of this, both the material conversion in the kiln system and the operational specifications of the overall process are influenced. The technology offers an additional degree of freedom for the process dimensioning in terms of the recirculation rate and oxygen concentration. Based on the outcome of phase II and the developed plant layout, open questions emerged regarding the applicability of oxyfuel technologies. Therefore, the research agenda of the subsequent phase III consisted of eight different work packages focussing on the most critical issues.

The essential issue of constant product quality has been proven in laboratory tests. In this context, different clinkers were burned under oxyfuel conditions in a laboratory oven and were used for the production of cement samples. Testing of the cement characteristics resulted in only slight variances (below 3 %) in properties like strength development and compressive strength compared to standard cements. According to this, negative impacts of oxyfuel combustion on the product quality seem to be negligible. In an analogous manner, the durability of basic and non-basic refractory material under oxyfuel conditions has been investigated. Brickwork consisting of basic material withstood the modified burning atmosphere, while the non-basic material showed a higher degree of thermo-chemical attack during oxyfuel treatment.

Investigations on the electric energy consumption of oxyfuel technologies identified the CO₂ purification unit (CPU) as a major cost factor. Depending on the flue gas conditions, namely volume flow, composition, temperature etc., the false air ingress becomes an important factor for the CPU performance. For this purpose, a techno-economic analysis examined the cost development with regard to different degrees of false air ingress and the resulting degree of impurities. Basically, varying the input CO₂ purity in the relevant range of false air resulted in a lower cost increase than enhancing the output CO₂ purity for transport and storage to 99%. With regard to the CPU performance, suitable concepts for sealing optimisation have been developed. According to these, complex solutions like waste gas flushed and suction-based systems could significantly reduce the ingress of false air. Based on the localisation of the main origin (poke holes, inspection doors, etc.), an improved maintenance of these devices was identified as a sufficient measure in terms of improving the CPU performance.

Based on the layout of a full oxyfuel cement plant, two design-related aspects in particular have been examined. In general the switching from conventional to oxyfuel conditions without adaptation of the burner design would result in significant changes in clinker quality due to a flame on a lower temperature level and higher gas velocities. However, an adjustment of the burner design and the associated parameters to the oxyfuel conditions could re-establish flame characteristics comparable to those of conventional conditions. Another notable fea-
ture of the plant layout is the two-stage clinker cooler. The required gas-tightness of the two stages, which are operated with different gas atmospheres, could be matched by two possible design concepts. Both concepts rely on the separation of the stages by dynamic devices in the hot clinker zone. With reference to a potential retrofit, a concept using two heat shields has been selected as the most promising solution.

Furthermore, the specifications of oxyfuel operation have been optimised by process modelling on the basis of the design specifications. In order to increase the overall efficiency, the integration of waste heat recovery aggregates like heat exchangers or aggregates for electricity production gain in importance. The waste heat utilisation can be matched to the specifications of the kiln plant (e.g. raw material moisture) resulting in a maximum raw material drying potential of 6.5 % and ~ 9 kWh/t of clinker power generation. Based on a recirculation rate of 0.57 the operational parameters have been adjusted to a stable operation without significant modifications of the kiln plant. Basically, the capture rate is at least 89% and at maximum 99% (at higher electrical input).

Summarising the results of the work packages, a reliable and sophisticated concept for the constructional realisation of an oxyfuel cement plant was developed. As the construction of greenfield cement plants is unlikely in Europe and more conceivable in fast developing countries, it might become important to offer solutions for retrofitting existing plants. Therefore, the concept has been evaluated with regard to the ability for retrofits. In general only a few modifications of the plant technology had to be implemented and the necessary redesign of plant components (cooler, burner) does not set limits for the retrofitting. A prerequisite of the retrofitting is however sufficient space in the surroundings of the plant. The conventional way of operating a plant does not have to be completely adapted (e.g. trouble-shooting). In conclusion it can be stated that the operation of an oxyfuel cement plant would not differ completely from that of a conventional plant.

In comparison to the developed full oxyfuel concept, the integration of partial oxyfuel was investigated by process modelling on a smaller scale. The simulations of the partial oxyfuel technologies gave a good overview of the corresponding energy efficiencies and the capture rates. Both concepts include certain modifications of the kiln plant, but would allow a retrofit of existing plants in principal. Although costs for electricity are lower using the partial oxyfuel due to the minor volume streams of flue gas and required oxygen, the CO₂ abatement costs are higher due to a reduced capture rate of between 65 and a maximum of 75 %.

**Post-Combustion Capture**

Post-combustion carbon capture is a tail-end technique which is able to remove the CO₂ from the flue gas just before it is emitted through the stack. The most common technique for this post-combustion carbon capture is amine scrubbing technology. While this technology is state-of-the-art for certain processes like the CO₂ removal from natural gas, it is expected to be one of the first available carbon capture techniques for fossil fired power plants and large industrial applications like cement plants. For the further investigation of the amine-based post-combustion carbon capture process, two work packages were defined which focused on the general equipment dimensioning and possible degradation reactions of the CO₂ solvent. Two additional work packages focused on the development and design of pilot plant tests.

Based on numerical process modelling, the dimensions of the necessary absorption column were calculated to about 20 m in height. For a 3,000 tpd clinker kiln, a column diameter of
about 6 m is necessary. As the area is a function of the squared diameter, absorption columns with a diameter of about 10 m to 12 m would be sufficient even for the world’s largest cement plants if the CO₂ concentration is not diluted too much by false air.

Investigations on the amine degradation reactions have shown a moderate impact of flue gas impurities on the solvent stability. SO₂ concentrations in the flue gas should be kept below 10 ppm for the operation of an amine-based capture system, while ammonia or carbonate-based systems are less sensitive to SO₂. Other flue gas components and impurities did not show a critical impact on the solvent stability. The pilot plant project was commenced with a concept study for a test facility in a cement plant. The facility was designed to feed up to three pilot scale CO₂ capture plants with approximately 0.5 % of the cement plant’s flue gas stream in parallel. Within the following pre-engineering study, available pilot plants were identified and negotiations with project partners took place. A concept was made for the design, construction and operation of the pilot plants and all interfaces between the cement plant and the pilot test facility were defined. All relevant aspects were laid down in a design basis document. The next steps in the project could be the detail engineering and construction of the test facility.

In conclusion, the findings of phase III have provided answers to important questions which had so far been open. It was confirmed that post-combustion might be available at a given time. Oxyfuel technology would still require more research, even if it could be shown that it might be applicable at existing kilns, however not without major investments. Although this technology might be less expensive than post-combustion, the overall cost due to the investment for modification and the high energy cost once in operation leave the economic impact of CCS on the cement industry as open as before.

European Cement Research Academy GmbH

Volker Hoenig Helmut Hoppe Kristina Koring Jost Lemke
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