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Technical Report

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ECRA CCS Project - Report about Phase II

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1 Introduction

Climate protection seems to be one of the most important items on the worldwide agenda. All states are challenged to reduce their CO₂ emissions dramatically, focussing on the major CO₂ sources in their countries to contribute to ambitious reduction targets being worked out on a global level. It is unclear today, how these targets can be reached. In the long run, energy efficiency and the utilization of renewables seem to be the most sustainable way to tackle the global greenhouse gas emissions.

The European Community's objective is to limit the atmospheric temperature increase caused by climate change to 2°C. This can only be achieved, when the global CO₂ emissions could be reduced by 50% until 2050. However, it is obviously not possible to reduce the EU or world CO₂ emissions by 50% in 2050 with energy efficiency and renewables alone. Therefore also carbon capture and storage of CO₂ (CCS) is looked at as an option to contribute to the portfolio of reduction measures. CCS could provide 19% of the needed reduction in 2050 (see **figure 1-1**). The European policy goal is to make CCS applicable by 2020. However, it is unclear if CCS implementation will be technically feasible and economically viable at that time.

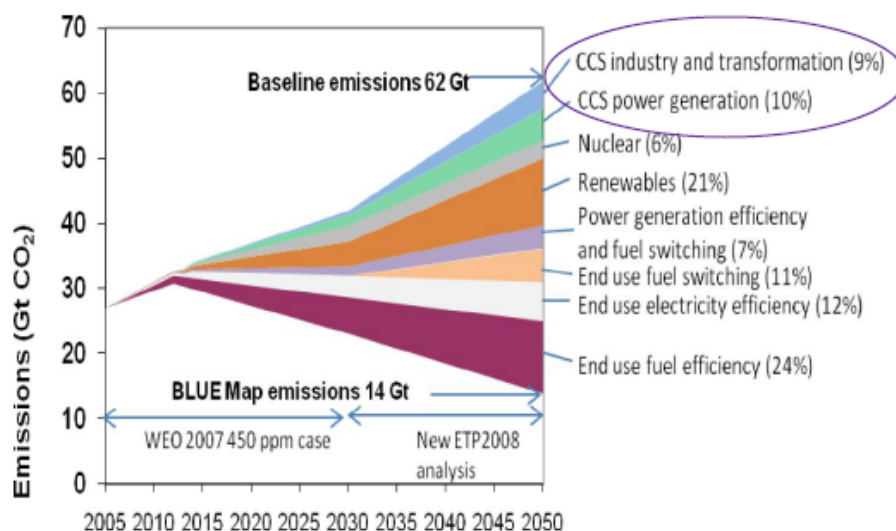


Figure 1-1: Portfolio of CO₂ reduction measures (Source: IEA, 2008)

Several industrial sectors have to be addressed to reach the targets for CO₂ reduction. The power sector is the most important CO₂ emitter. According to this many power companies around the world are already involved in CCS research, pilot projects or are even planning demonstration projects. Besides that, also other industrial sectors with significant CO₂ emissions like the cement industry have to contribute to the global activities to reduce the CO₂ emissions. The International Energy Agency (IEA) predicts that 1.4 Gt of CO₂ have to be captured from the cement industry by 2050 [van Puyvelde, 2008]. According to this, 50% of the European cement works would have to apply CCS measures. The IEA vision for 2030 is

that 30 cement works in Europe would apply CCS (and 70 more in the rest of the world). Therefore there is a need for early research activities on CCS also in the cement sector.

To initiate this new field of research, ECRA's Technical Advisory Board and the CCS Steering Group set up the structure for a long-term research project on CCS, which comprises five phases. Each of the phases requires the deliverables of the previous phase. Whenever a new phase will be started, this has to be initiated by the Technical Advisory Board based on the decision to continue the project, to redefine or even terminate it. The phases as they are seen today can be summarized as follows:

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

Phase I was finalized in spring 2007 and provided a first overview of CCS and its potential implications which can be foreseen for the cement industry. The report is available to the general public and can be downloaded from ECRA's website (www.ecra-online.org). It includes an evaluation of pros and cons of potential application in the cement industry. At the end, four options to capture CO₂ were identified: pre-combustion, post-combustion, oxyfuel technology and carbonate looping. Although a detailed technical understanding of CCS is still pending, the study concluded that today all capture technologies are far from being applicable to the cement industry due to technical and cost reasons. In general, avoidance costs of up to 40 to 50 € per ton of CO₂ can be expected for CO₂ capture (including transport and storage costs) and it is clear that such costs would have a severe impact on the competitiveness of the cement industry.

The Phase I Report resulted in the conclusion that some capture technologies are more appropriate for the potential application at cement kilns than others. This applies to oxyfuel and post-combustion technology. Consequently the ECRA Technical Advisory Board and the Steering Group to the CCS study decided to continue the project and launch Phase II in order to look at these technologies in a feasibility study in more detail. Phase II is financed by the ECRA members and industrial partners willing to contribute and to benefit from the discussions within the project team.

Phase II of the CCS research project was started at the end of 2007 and will be completed in summer 2009. The main objective in this phase was to perform a feasibility study of CO₂ capture for the clinker burning process which focuses on oxyfuel and post-combustion measures. Apart from technical investigations and assessments, an economic analysis will also be included in the report.

It is not clear at this time how the CCS project will be continued after Phase II. However, since subsequent phases of the CCS research project will include laboratory tests and pilot-tests, public funding will be indispensable. According to the project schedule, Phase III of the research project shall last from autumn 2009 until summer 2011. The main research tasks would be running laboratory-scale tests with different chemical absorbents and with typical cement kiln exhaust gas mixtures and furthermore simulating the capture processes. In this project phase, cooperation with universities, research organisations and specialist companies is desired.

The last project phase (Phase IV) is dedicated to pilot-scale trials which have to be carried out to gain real-case experience. The pilot tests should demonstrate the reliability and effectiveness of capture processes. From today's perspective this project phase could be started not before summer 2011 and should last 2 or 3 years. The execution of the associated work packages would require cooperation with leading equipment suppliers or major licensors of capture technologies.

As mentioned before the application of capture technologies would be a very demanding objective for the cement industry. It can be seen as an example for precompetitive joint research. A successful completion of the research project would enable the cement industry and its equipment suppliers to make scientifically sound decisions to meet future challenges regarding CO₂ reduction.

The current report shall give a more detailed view on the potential application of oxyfuel and post-combustion technologies at the clinker burning process. Furthermore, a current overview about other CCS issues is given, like CCS activities in the power sector, CCS legislation, transport and storage of CO₂.

2 International research activities on CCS and CO₂ reduction

According to international agreements on European and worldwide level, significant CO₂ reductions have to be achieved in the next years. Therefore, extensive research work about CO₂ reduction is being carried out all over the world. Some billion US-\$ are provided worldwide for funding of the current research work. The next chapters give a short overview the current activities.

2.1 Research activities in the power sector

Power plants are the most important industrial CO₂ sources. Therefore most of the current CCS pilot and demo projects are being carried out in the power industry. The focus of those projects is on the "conventional" technologies, which means post-combustion (chemical absorption), oxyfuel and pre-combustion (namely IGCC). In the later **chapters 3.4.2** and **4.2.1** an update about current CCS research activities in the European power sector is given, including pilot and demo projects. Other technologies which are only developed on research level are not included in any pilot project and are not seen as commercially available in the next 10 or 20 years.

2.2 Future technologies

Extensive research is carried out worldwide not only about CO₂ capture, but also about CO₂ reduction and transformation of CO₂ into hydrocarbons, alcohols like methanol or ethanol or CO and H₂ respectively. In most cases sophisticated catalysts are used to achieve the desired reaction products. Hydrocarbons or alcohols be used as "biofuels", whereas CO / H₂ mixtures could be fed into fuel cells [Grimes, 2009], [Azad, 2009] [Reuters, 2009/2].

The use of algae is also tested to bind CO₂ from combustion processes. The world's most progressive algae growing plant, which is operated by the power company RWE at Niederaußem, is used to examine opportunities for CO₂ use. The goal is to optimize the entire process chain from seaweed production to the final product. In a trial plant, which is measuring some 600 m², the seaweed is "fed" with flue gas from the power plant. For the resulting algae biomass, possible uses are to be investigated, e.g. as biofuel.

However it is expected, that those technologies can become only a small piece in the big CO₂ reduction puzzle. It is unclear how these processes could be scaled up to reduce the billions of tons CO₂ which are produced annually by burning fossil fuels.

2.3 Research activities in the cement sector

In contrast to the power sector, where many CCS pilot and demonstration projects are being planned, the cement industry is still in an early state of CCS implementation into pilot or demonstration projects. Apart from the ECRA CCS project, other studies, trials and theoretical assessments about the potential application of CCS measures in the cement industry have been carried out.

IEA / BCA:

On behalf of the International Energy Agency (IEA) and the British Cement Association (BCA) the consultant Mott MacDonald provided a study about CO₂ capture in the cement industry [IEA, 2008].

Furthermore the cement producer Lafarge SA announced a plan to take part in Britain's future carbon capture and storage infrastructure. The captured CO₂ shall be stored in depleted oil and gas fields in the North Sea [Reuters, 2009].

CO2CRC:

The Cooperative Research Centre for Greenhouse Gas Technologies (CO2CRC), which is based in Canberra (Australia), is one of the world's leading collaborative research organisations focused on carbon dioxide capture and geological sequestration (CCS). The cement industry is one of the major CO₂ emitters in Australia and therefore seen as future user of carbon capture technologies.

CO2CRC has announced a detailed study about various options for CO₂ capture from the clinker burning process [van Puyvelde, 2008]. The study shall be used for the discussions about 20 demonstration projects which could be funded by the G8 countries [van Puyvelde, 2008].

WBCSD / CSI:

A study "Development of State of the Art-Techniques in Cement Manufacturing: Trying to Look Ahead" was commissioned by the Cement Sustainability Initiative (CSI), a member-led program of the World Business Council for Sustainable Development (WBCSD) [CSI, 2009]. The report represents the independent research efforts of the European Cement Research Academy (ECRA) to identify, describe and evaluate technologies which may contribute to increase energy efficiency and to reduce greenhouse gas emissions from global cement production today as well as in the medium and long-term future. While the results have been reviewed by ECRA and CSI member companies and stakeholders like the International Energy Agency (IEA), the opinions and views expressed are those of ECRA. The study contains state-of-the-art descriptions both for conventional technologies for CO₂ reduction and also papers about the different CCS technologies.

Cansolv:

J. Sarlis and D. Shaw presented the Cansolv activities about amine scrubbing on the 11th Workshop of the Post-Combustion Network in Vienna [Sarlis, 2008]. According to that, in January and February 2008 a trial was carried out at a cement kiln of California Portland (California / USA), during which a 90 % removal rate for CO₂ was achieved. However, there is no more information available about the detailed results of the trial.

DVV / VDZ:

A method of capturing CO₂ uses a "carbonation-calcination cycle", whereby CO₂ is removed from the flue gas via a chemical reaction with calcium oxide and – as a result of it - CaCO₃ is produced. The CaCO₃ is then heated to a high temperature to start a further reaction which separates out the CaO and CO₂. This produces concentrated CO₂ gas which is suitable for CO₂ storage. The degenerated absorbent could be used as secondary raw material in the cement industry. In principle, the Carbonate Looping Process could also be used for CO₂ reduction at the clinker burning process.

The German Combustion Research Association (DVV) and the Research Institute of the Cement Industry have submitted a joint application for a research project about "carbonate looping" to the German Federation of Industrial Research Associations.

Novacem:

Novacem, a spin-out from Imperial College, London, developed a cement based on MgO and special mineral additives. The production causes minimal CO₂ emissions and requires lower temperature processing. It hardens by absorbing atmospheric CO₂ [Novacem, 2009]. No detailed information about the consistence, production process / performance is available so far.

Calera:

The idea of the Calera process is that CO₂ is bound into a product called "calcium carbonate cement" [Biello, 2008]. The process imitates the formation of "marine cement" by corals which are taking calcium and magnesium from the seawater to build their shells and reefs. It is claimed that for every ton of "cement", half a ton of CO₂ is sequestered, so that it would be an effective measure for CO₂ capture and storage.

To produce the "calcium carbonate cement", only seawater and flue gas containing CO₂ is needed. The waste heat of the flue gas is used for drying the resulting slurry. The final product is calcium carbonate. No reference is made to the cementitious characteristics of this material.

3 Post-combustion CO₂ capture

3.1 General update

Post-combustion CO₂ capture covers various concepts for the end-of-pipe carbon dioxide abatement. While some techniques are only subject to basic research (i.e. membrane gas separation¹), amine based absorption techniques are already used as a state-of-the-art technique for natural gas sweetening and CO₂ production [Kohl, 1997]; [IPCC, 2005].

During the past years, absorptive post-combustion CO₂ capture has become an emergent technique for greenhouse gas sequestration. By now, post-combustion projects account for more than 50 % of all carbon-capture demonstration projects that shall go into operation between 2010 and 2015. It is expected that post-combustion capture will be commercially available for the power sector after 2020, at least by technical means [ZEP 2008].

Current pilot and demo plants for post-combustion capture are solely based on chemical absorption. Amine based systems cover the major part of all projects; however the chilled ammonia process is employed in some pilot trials, too. The main reasons for the employment of absorptive post-combustion capture are:

- Possible CCS-retrofit of nearly all CO₂ point sources
- Large scale availability
- Very little impact on combustion/production process
- CO₂ stream with high purity (>> 99 % v/v)

The disadvantage of this concept is its high energy consumption. Approximately 3000 kJ of heat are used to separate 1 kg of CO₂ from the gas stream and the heat supply usually causes emissions, too. This energy/CO₂ penalty decreases the effectiveness of the capture process, though the huge energy consumption for solvent regeneration still dominates research and optimization efforts. New solvents and optimized process concepts are discussed but no break-through has been achieved so far.

3.2 Unit operations

The main unit operations of post-combustion CO₂ capture are the absorber and desorber columns, the reboiler and the CO₂ compression unit (see **figure 3-1**). The actual capture process happens in the absorber column where the liquid solvent reacts with CO₂ from the gas phase. The CO₂-rich solvent then is transferred to the desorber column and heated up. In the desorber, the backward reaction occurs and CO₂ is released into the gas phase. The solvent is returned to the absorber while the CO₂ is dried and compressed for further transport and storage. The solvent at desorber bottom is heated up with a steam-fed reboiler; additionally coolers and heat exchangers are employed to control the temperature levels.

¹ an update on recent developments with membrane technologies is given in chapter 3.9

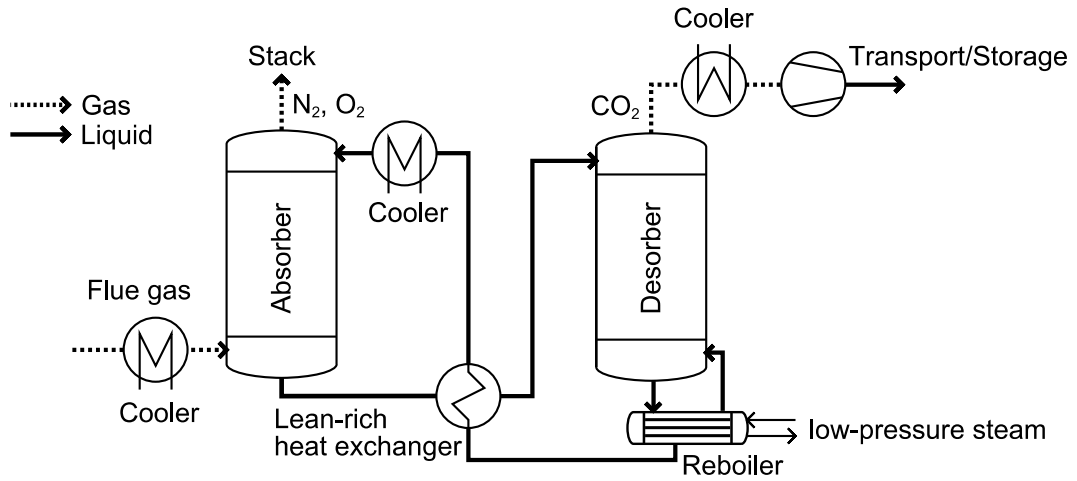


Figure 3–1 Basic design for absorptive CO₂ capture

The solvent’s CO₂ capacity mostly depends on its vapour-liquid equilibrium (VLE) which is related strongly to CO₂ partial pressure and temperature. **Figure 3-2** shows how the capacity is obtained, this differential capacity between lean and rich solvent is called ‘pick-up range’. In addition, the rate of reaction plays an important role how far the equilibrium can be achieved within the real process.

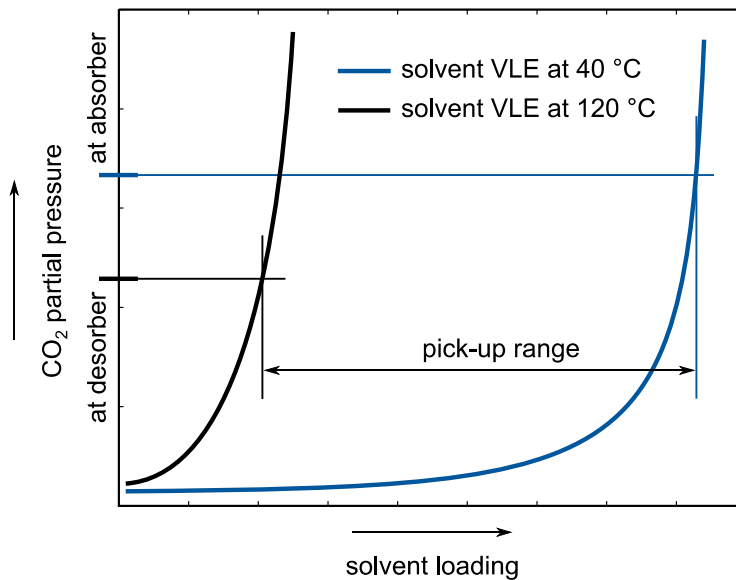


Figure 3–2 Pick-up range of solvent between absorption and desorption temperature

3.3 Results of R&D (last 2–3 years, state of the art / pilot trials)

Since the Phase I report in 2007, a lot of scientific work was published, especially at the Conference on Greenhouse Gas Technologies (GHGT) and the International Network for CO₂ capture that is part of the IEA Greenhouse Gas Research Programme. The work focuses on three major aspects:

- new solvent systems
- optimization of process design
- pilot projects

3.3.1 Existing and new solvent systems

The published research of the last few years shows various efforts to find new, cost and energy effective CO₂ solvents. But most substances do not match the requirements for effectively replacing established solvents like monoethanolamine (MEA), methyldiethanolamine (MDEA), or aminomethylpropane (AMP). Most plants use monoethanolamine or proprietary amine mixtures like aMDEA[®] (BASF) or KS-1 (MHI/KEPCO). These amine blends are sometimes considered as second generation solvents in contrary to the first generation (i.e. pure MEA) (see **table 3-1**) for a brief summary of common solvents and new solvent concepts for more energy efficient absorption systems.

Table 3–1 Solvent chemicals for CO₂ absorption

Code	Chemicals	Reboiler duty in [kJ/kg CO ₂]
<i>proven and commercially available</i>		
MEA	monoethanolamine	3,000...4,000
KS-1	sterically hindered amine	2,600...3,500
aMDEA	piperazine/tertiary amine	...2,600...
<i>promising candidates</i>		
AC	NH ₃ /(NH ₄) ₂ CO ₃	(2,000...3,000?)
PZ/KC	piperazine promoted K ₂ CO ₃	(3,250...3,500?)
IL	ionic liquids	basic research (mid term)
EZ	enzymatic solvents	basic research (long term)

The selection of solvents is done with respect to three main aspects:

- thermodynamics and kinetics
 - low desorption enthalpy
 - high CO₂ capacity, large 'pick-up range'
 - high absorption rate constant
 - low vapour pressure
- chemical reactions that are not related to CO₂
 - resistance against degradation
 - risk of equipment corrosion

- general properties
 - toxicity and biodegradability
 - solvent cost

Another feasible approach to effective post-combustion capture is the chilled ammonia process (CAP). An ammonia/ammonium carbonate-solution is used for CO₂ absorption. During the capture process, ammonium bicarbonate is formed and precipitates as a solid. The technique was patented in 2006; in 2008 the first pilot plant went into operation in Wisconsin, U.S. [Freeman, 2008].

Basically, the chilled ammonia uses the same approach to carbon capture as the amine based process does; there are, however, significant differences: The chilled ammonia process uses a fugitive solvent (NH₃) and requires a complex wash section in the column heads including a small extra desorber for treating the effluent from overhead wash section. The flue gas is cooled down to less than 10°C at the absorber inlet, thus additional refrigeration capacities are necessary. Furthermore, ammonium bicarbonate precipitates in the solution of the rich solvent. It has to be separated with a hydro cyclone from the circulating solvent [Gal, 2006].

Table 3–2 Pros and cons of CO₂ solvents

Solvent	Pros	Cons
MEA	proven concept high absorption rate	energy consumption degradation
aMDEA	proven concept high absorption rate lower energy consumption	more expensive than MEA degradation proprietary system
other proprietary amines	proven concept high absorption rate lower energy consumption increased degradation resistance	more expensive than MEA degradation proprietary system
chilled ammonia	cheap solvent insensitive to gas impurities low reboiler duty	refrigeration facilities needed ammonia slip different equipment required low absorption rate constant

3.4 Current R&D topics

3.4.1 New solvent systems

Commercial available solvents are grouped into ‘first generation’ and ‘second generation’ solvent systems. Solvents of the first generation are binary mixtures of water and amine or water and inorganic salt as monoethanolamine (MEA), diethanolamine (DEA), triethanol-

amine (TEA) or potash (K_2CO_3). While especially MEA plays still an important role, blended alkanolamines (second generation solvents) are used to increase the absorption rate constant and to lower the regeneration energy.

Results from basic research suggest two subsequent classes of even more efficient solvents [Feron, 2008]:

- ionic liquids (IL) "third generation"
- enzymatic solvents (EZ) "fourth generation"

Ionic liquids are fused salts that stay in liquid state at ambient temperature; they show very low vapour pressures. Some ionic liquids react selectively with CO_2 and are suited for CO_2 -capture in general. However, despite their selectivity, known ionic liquids do not exhibit relevant CO_2 loadings to compete with available alkanolamines.

Proposed *enzymatic solvents* are based on the same principles that are used for biological CO_2 fixation. It is suggested that enzymatic solvents may offer nearly optimal energy efficiency for CO_2 absorption, however both, ionic liquids and enzymatic solvents are still subject to basic research and will not be available for the commercial ramp-up of CO_2 -capture systems.

3.4.2 Process design

The usual set-up of a chemical absorption system consists of two columns (absorption and desorption) and a reboiler for solvent heating. The columns are filled with a random packing to achieve a large gas-liquid interface. Additional cooling and heat-exchanging devices are required to keep the solvent at optimal temperature. Research suggested many improvements to this basic concept and some of them are state-of-the-art by now:

- Structured packing
- Interstage cooling
- Flash evaporation and lean vapour recompression

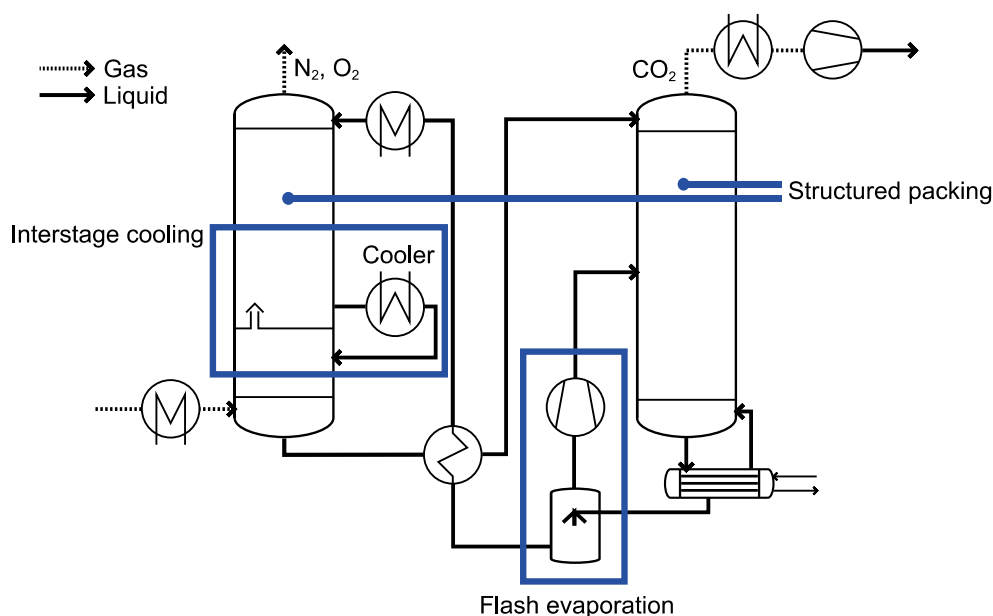


Figure 3–3 Amine based CO₂ absorption with state-of-the-art process

A metal packing is used in the columns to produce a large gas-liquid interface. *Structured packing* shall optimize the useable packing surface and to lower the pressure drop between column bottom and head section.

The exothermal absorption process increases the solvent temperature and impairs the chemical equilibrium between solvent and CO₂. An *interstage cooling* system improves the temperature profile in the absorption column and leads to a higher solvent loading.

A *flash evaporation* tank with subsequent vapour recompression benefits from the slightly higher desorber pressure. The solvent pressure drops from ca. 1.5 bar to nearly ambient conditions and causes the release of further CO₂. The vapours are recompressed and piped to the desorber while the solvent continues to the lean/rich-heat exchanger.

3.4.3 Pilot and demo projects

Pilot and demonstration projects are needed to gain more knowledge about post-combustion CCS. For Europe it can be asserted that the power industry is planning several demo projects in different countries. Many of them are post-combustion projects, namely chemical absorption processes. To prepare the demo projects, several pilot projects were carried out or are planned for the near future. Some of the pilot projects were supported with public funding.

In 2006, the first European pilot plant for post-combustion CO₂ capture was commissioned at a coal-fired power station in Esbjerg, Denmark (Dong Energy). The pilot project operated in four testing campaigns [Knudsen, 2007]. The plant was modified after the CASTOR project and is part of the next project called CO₂CESAR, which started in February 2008 and which

is funded by the EU 7th Framework Programme. The total budget of the CASTOR project was about 15 Mio. €. The investment costs for the pilot plant was less than 2 Mio. €. In March 2009, an ECRA group had the possibility to visit the Esbjerg power station and to discuss with the plant personnel about the present experiences with the pilot plant.

The CASTOR pilot plant is designed to handle 5,000 cubic meters (stp) of flue gas per hour, capturing about 1 ton of CO₂ per hour at 90 % CO₂ separation efficiency. The columns cover 1.1 m in diameter and have a height between 25 m and 30 m. This setup allows first assumptions for dimensions of full-scale plants.

During 2009, a second post-combustion pilot plant is in commissioning at the Niederaußem lignite fired power plant of RWE AG. This pilot project is a joint-venture of RWE, Linde, and BASF; it shall use MEA and aMDEA as solvents. The project is co-funded by the German Federal Ministry of Economics and Technology (BMWi) [Moser, 2008].

In the framework of the ECRA CCS project, there was a further meeting with RWE in September 2008 about the Niederaußem pilot project and another one with Vattenfall about their CCS projects (especially storage). It was agreed to stay in contact and to exchange experiences about current CCS activities.

Table 3–3 gives an overview about European post-combustion pilot and demo projects, which shall be conducted in the next years. It can be expected that some of the results obtained in the power sector can be transformed also to post-combustion pilot plants at cement kilns.

Table 3–3 Announced post-combustion pilot and demo projects in Europe [ZEP, 2008]

Company	Partner / Equipment Supplier	Location / Country	Pilot / Demo	Start
DONG Energy (CASTOR)	TPI Curno / Italy	Esbjerg / Denmark	pilot	2006
ENEL / ENI		Brindisi / Italy	pilot	2009
EON	Siemens	Staudinger / Germany	pilot	2009
EON	Cansolv	Heyden / Germany	pilot	
EON	Fluor	Wilhelmshaven / Germany	pilot	2010
EON	Alstom	Karlshamn / Sweden	pilot	2009
EON TNO	TPI Curno / Italy	Massvlakte / Netherlands	pilot	2008
EON		Kingsnorth / UK	demo	?
EON	MHI	N.N. / Germany	pilot	?
Gassnova		Karstø		
RWE	Linde, BASF	Niederaußem / Germany	pilot	2009
RWE npower	TPI Curno / Italy	Didcot / UK	pilot	2008
RWE npower		Tilbury		2016
Scottish and Southern Energy		Ferrybridge		
StatoilHydro	Aker Clean Carbon	Mongstad		2011
Vattenfall		Jänschwalde / Germany	demo	2015
Vattenfall		Nordjylland / Denmark	demo	2013

3.5 Research activities within the ECRA project

3.5.1 General understanding of thermo-chemical mechanisms

The fundamental concept of absorptive carbon capture implies a chemical solvent that reacts with CO₂ in a selective, exothermal, and reversible way. The selectivity is of most importance for achieving a pure CO₂ stream. Furthermore a reversible reaction is necessary to separate the CO₂ and for reusing the solvent. While a high absorption enthalpy ΔH_{abs} leads to a high loading of the solvent and a driving force to the absorption reaction, it also increases the necessary energy for regeneration. Hence, solvents with well balanced equilibrium and kinetic parameters are necessary to provide an energy efficient capture process.

The transfer of CO₂ from the gaseous to liquid bulk is described by Whitman's Two-film Theory (see **figure 3-4**). The highest resistance to the CO₂ transfer is expected at the liquid film interface, this section is subject of detailed modelling. The CO₂ gradient in the gas film and the heat gradient are considered to be nearly constant [Tobiesen, 2007].

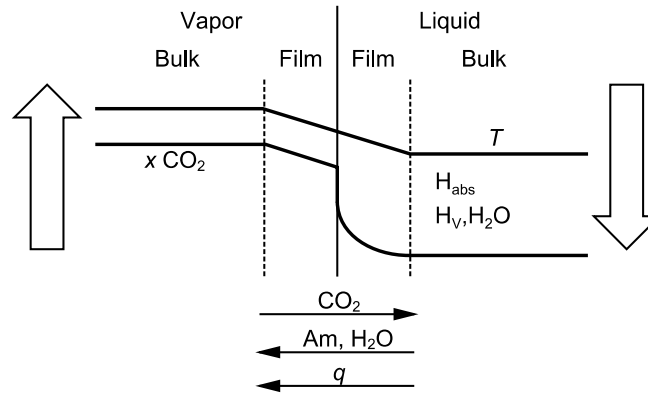


Figure 3-4 Whitman's two film model, representing the mass transfer at a gas-liquid interface

3.5.2 Flue gas characteristics

To provide a reliable data basis for subsequent modelling studies, a cement kiln flue gas specification was used. Based on usual fuel compositions and energy consumption data, possible gas concentrations were defined in the ternary system of N₂, O₂, and CO₂. Concentration of water vapour strongly depends on the mode of operation and the raw material moisture. The role of different water concentration is marginal as the flue gas is cooled down below 40 °C at the absorber inlet. Due to the lowered dew point and the direct cooling, the gas stream is saturated with water in any case. At 40 °C, the concentration of water vapour is about 7 % (v/v). If a lower flue gas temperature is required, i.e. for the chilled ammonia process (0 °C...10°C), the water content is even lower, usually less than 1 % (v/v). **Figure 3-5** shows the range of possible flue gas composition.

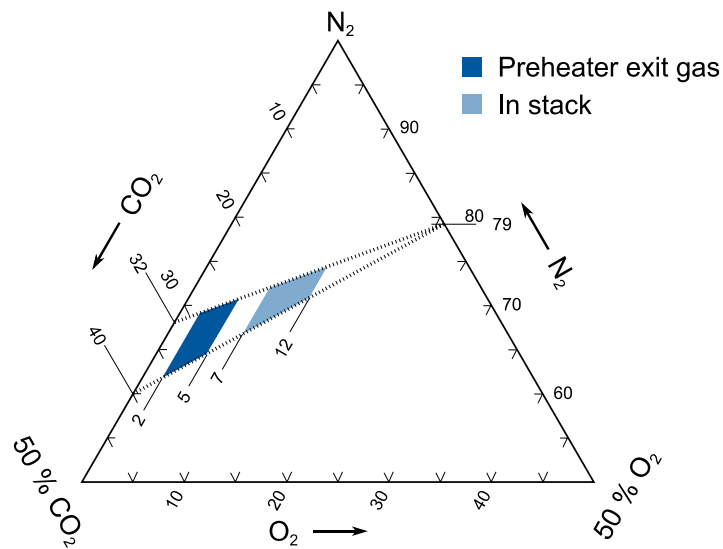


Figure 3-5 Dry gas composition of cement kiln flue gas after pre-heater and in stack

Other flue gas constituents with relevance to the carbon capture process are sulphur dioxide, nitrogen dioxide, and carbon monoxide. The sour gases react with organic solvents and cause the formation of heat stable salts and degradation of the solvent, leading to increased emission of ammonia.

The most critical gas component is SO₂; it reacts nearly completely with the solvent. Thus, SO₂ limits below 30 mg/m³ were suggested in different publications, so far. Other studies conclude that SO₂ levels of 90 mg/m³ respectively 140 mg/m³ are still acceptable.

NO₂ concentration shall not exceed 40 mg/m³. As NO₂ usually accounts for not more than 5% of total NO_x in cement kiln flue gases, a reduction to 800 mg/m³ or less will be necessary. Carbon monoxide reacts rather slowly with amine solutions, it is likely but not verified that CO is irrelevant for notable solvent degradation.

An evaluation of all German cement kilns showed that the average NO_x-concentration is quite evenly distributed around 410 mg/m³ (+/- 24 mg/m³) in contrary the distribution of SO₂ emissions shows that most plants emit very little SO₂ (> 50 % below 100 mg/m³). This evaluation takes only the German cement kilns into account, it can be expected that the general distribution characteristics do not differ significantly from other countries while the distribution parameters may change (see **figure 3-6**).

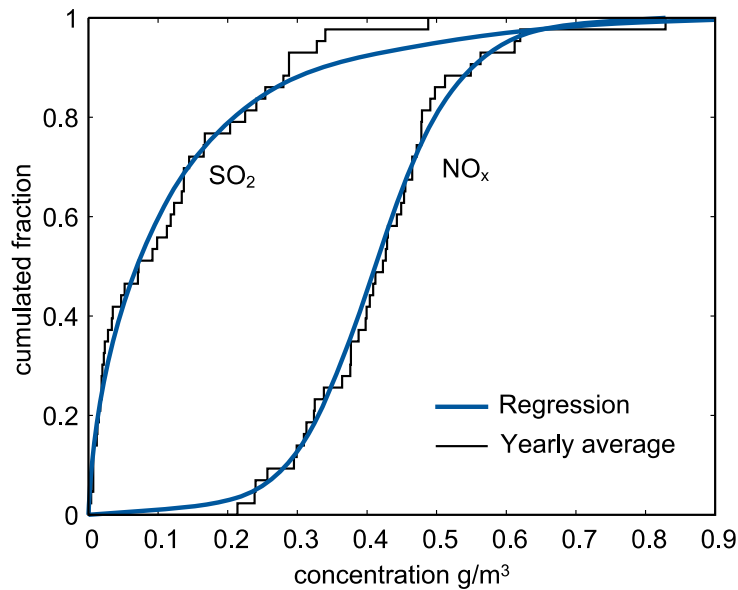


Figure 3–6 Distribution of SO_x and NO_x in cement kiln flue gases (43 plants, Germany, 2007)

The flue gas' dust loading is suggested to be less than 10 mg/m³. This condition is achievable but requires the use of state-of-the-art fabric filters.

3.5.3 Concepts for implementation of post-combustion capture

End-of-pipe measurements imply the advantage that they are easy to connect with the existing process. Installing post-combustion carbon capture at a clinker burning site would need the replacement of the stack by the carbon capture equipment, leaving all other components of the plant unchanged. **Figure 3-7** shows an exemplary process flow diagram.

Rough estimations on equipment sizes are possible with data from pilot trials. Based on the Esbjerg pilot plant, an absorber for a 3000 tpd cement kiln would be about 30 m high and 6 m to 8 m in diameter with a flue gas velocity of about 1.5 m/s. The desorber is expected to be smaller size, approximately 25 m high and between 4 and 6 m in diameter.

It is estimated that a cement kiln including carbon capture would consume as much as twice the energy of an actual state-of-the-art facility. Due to the huge energy consumption of the capture process, all existing and utilizable sources of heat have to be used to cover the solvent regeneration. In addition, supplementary heat or power generation is mandatory to satisfy the energy demand.

Cement kilns exhibit a very high thermal efficiency ($> 65\%$) and a high specific CO_2 emission footprint per fired fuel energy ($> 0.25 \text{ t/GJ}$) due to the large amount of carbon dioxide that is released during the calcination of limestone. These two facts cause that not more than 15 % of the required reboiler energy could be extracted from the clinker burning process. For example, heat extraction from the process of 300 kJ/kg clinker would satisfy about 12 % of reboiler duty for the corresponding CO_2 capture, based on a reboiler duty of 2500 kJ/kg CO_2 and a CO_2 emission factor of 1kg/kg clinker.

To complete the dilemma, an additional power plant would cause CO_2 emissions itself. **Figure 3-8** explains this relationship for a coal-fired power plant: Assuming a required abatement rate of 80 % and an overall energy consumption of 4,000 $\text{kJ}_{\text{th}}/\text{kg CO}_2$, the plant has to capture 88 % of the flue gas stream from the cement kiln and the power plant. The latter one needs a capacity of at least 62 kW_{th} per ton of daily CO_2 emission from the cement kiln. A 3,000 tpd kiln with 0.8 kg of CO_2 per 1 kg clinker would need a 150 MW power plant in this case.

Unless the energy demand could be satisfied by waste heat from a nearby existing facility, an expansion of local power supply is necessary. In any case, an integrated solution for energy supply is required. **Table 3-4** shows different ideas how the energy could be supplied.

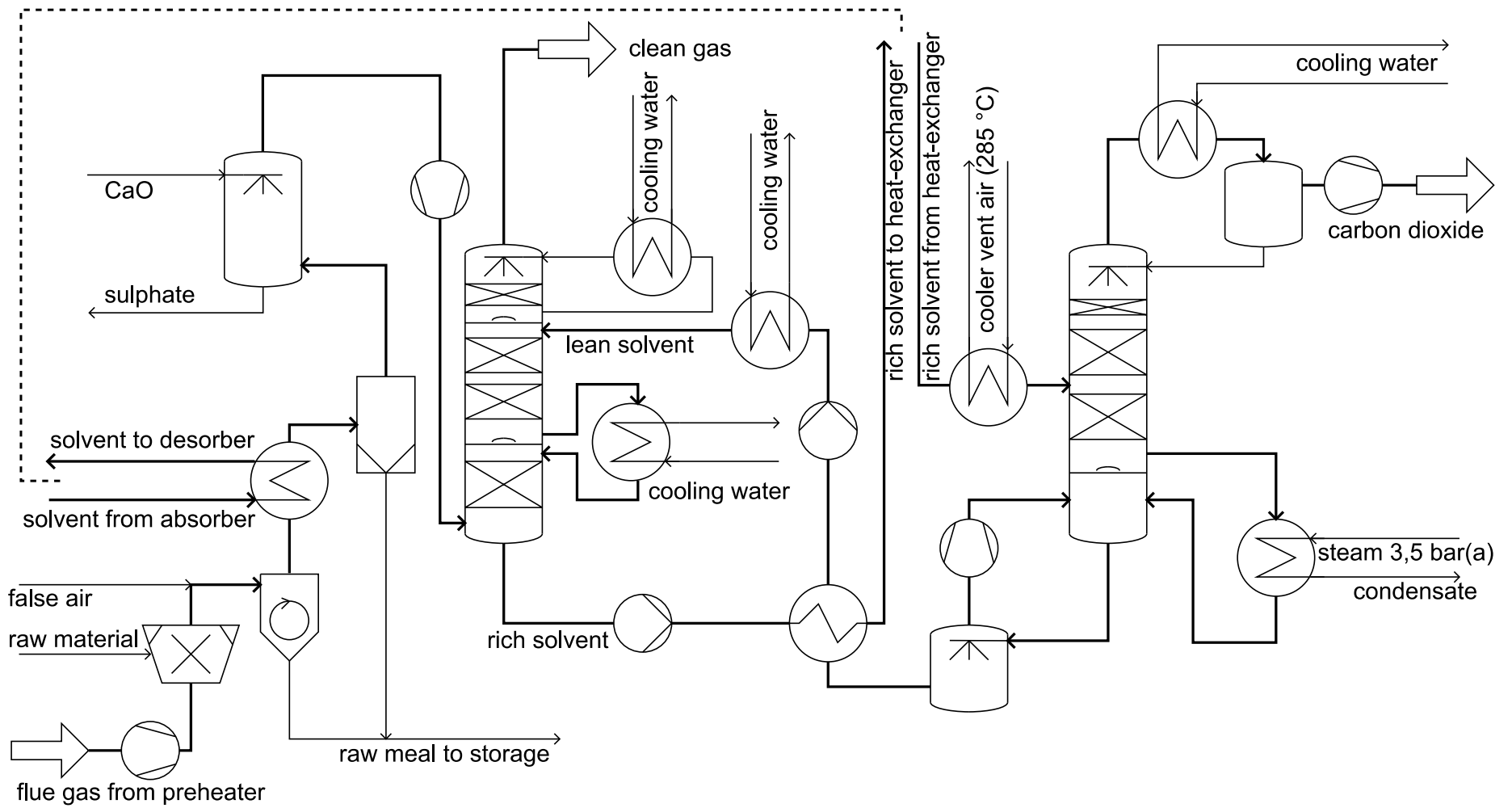


Figure 3–7 Possible implementation of post-combustion capture to the clinker process, including deSOx if required

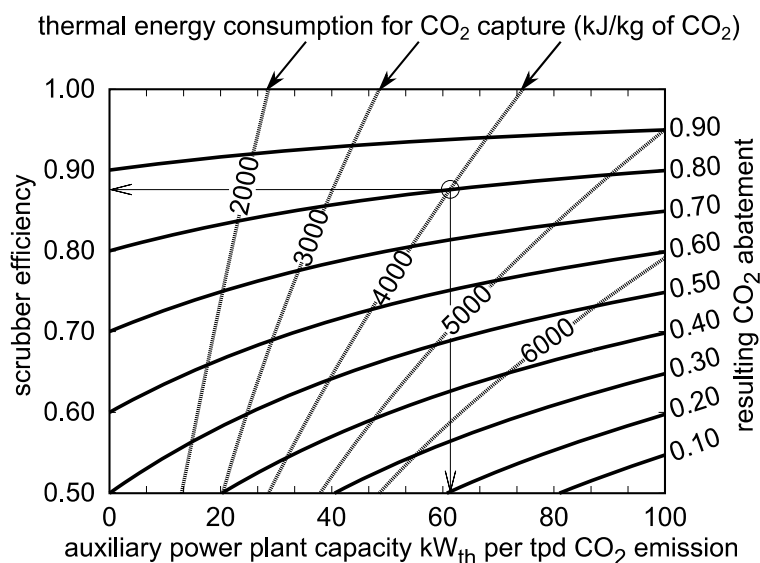


Figure 3–8 Decay of CO₂ abatement due to energy penalty and related additional emission (coal fired auxiliary power plant)

The simplest way is a separate auxiliary power plant of which flue gas is emitted into the atmosphere. This concept would cause minimum construction efforts but allow only a CO₂ abatement of 55 % related to the clinker specific emissions. The abatement rate could be higher if i.e. gaseous fuels are used which result in lower specific CO₂ emissions than coal. In this case, up to 70 % of the clinker process could be sequestered without treating the flue gas.

Currently, the most feasible way seems to be the collective treatment of kiln and power plant flue gases in a larger CO₂ scrubber, but hybrid concepts with an oxyfuel based power plant could be even more energy efficient in the future. Additionally, an already CO₂-free reboiler heat supply would allow the highest rate of abatement. While this concept would be suitable only for sites with sufficient sources (i.e. biomass based, solar or geothermal energy), it offers a smart combination of available and sustainable techniques.

Table 3–4 Concepts for integration of an auxiliary power plant

Description	CCS technique		Approx. CO ₂ abated from clinker process
	Cement Kiln	Aux. Power Plant	
Separate	Post-combustion	None	55 %...70 %
Combined	Post-combustion (collective)		85 %...90 %
Hybrid	Post-combustion	Oxyfuel	85 %...90 %
Renewable	Post-combustion	Not necessary	90 %...95 %

3.5.4 Capture ready cement plants

First of all, a capture ready cement plant has to hold enough space for equipment construction available.

In comparison to power plants, the carbon capture process at cement plants will be less integrated. The main reason is the lack of available low pressure steam and cooling water. Cooling water is used for chilling the lean solvent, the wash sections at column heads and the separated CO₂. However cooling water is not absolutely necessary as fully air cooled CO₂ capture plants are available as well. In any case, large amounts of low pressure steam are necessary (approx. 1 t of steam per 1 t of clinker). Cement kilns that are already co-located with a power plant could get the steam from this source, but generally, a cement kiln with carbon capture will need a new auxiliary power plant.

3.6 Knowledge gaps / suggestions for further work

3.6.1 Modelling

To allow an in-depth evaluation of the absorptive carbon capture process, a complete and detailed modelling is needed. Rigorous models for absorption and desorption column are available, and tested against experimental data [Tobiesen, 2007], [Tobiesen, 2008].

3.6.2 Integration concepts

The concepts for integrating the capture process into a cement plant are still on a basic level. In combination with the modelling, more detailed evaluation is necessary to identify best concepts and possible decision strategies. The process modelling shall help to identify the most feasible and economic approaches.

3.6.3 Degradation / gas impurities

In general, there is plenty of literature on ethanolamine degradation available. During recent years, detailed work especially elaborated the mechanisms of oxidative degradation. On the contrary, a suitable guideline about acceptable gas impurities with consideration to the clinker specific flue gas composition is missing.

The concurrent influence of process-specific gas impurities should be investigated within an experimental study.

3.7 Cost estimates for pilot and demo trials

3.7.1 Pilot plants

In 2006, the first pilot plant was erected at Esbjerg coal fired power plant as part of the CO₂CASTOR project. The overall budget for the CASTOR project was 13 Mio. €. Thereof, 2 Mio. € were used for construction of the pilot.

The complete Niederaußem pilot project has a budget of about 20 Mio. €; the cost for this pilot plant is likely higher than in Esbjerg due to more complex process monitoring. Both

projects cover more tasks than just the pilot plant. It is roughly expected that a complete pilot project in the cement industry would cost between 6 and 12 Mio. €.

3.7.2 Full-scale / demo plants

Since 2004, different studies investigated the costs for installation and operation of a post-combustion carbon capture plant at cement works. An early study by Mahasenan et al. calculated operational costs between 40 € and 80 € per ton CO₂ (2004) for capture and storage at north-American cement plants. A detailed study from Norway, prepared by GassTek, estimated operational costs about 45 € per ton of CO₂ and capital expenditures of 110 Mio. €², including a seawater SO₂ scrubber and a natural gas-fired combined heat and power plant (power is used directly as shaft work, no electricity generation). This study is part of the most detailed work on this topic, so far. However, the presented concept is tailored to a certain Norwegian cement plant (ca. 3,300 tpd clinker); the numbers might not be representative therefore.

A more general study on carbon capture in the cement industry was prepared by the British Cement Association in 2008, and published by the International Energy Agency (IEA) [IEA, 2008]. This study concludes CO₂ abatement costs of approx. 100 € per ton of CO₂ and capital expenditures of approximately 300 Mio. € for a post-combustion capture installation including a coal fired combined heat and power plant [Hegerland, 2006]. Design basis is a state-of-the-art 3,000 tpd cement kiln. The capacity of the Norwegian plant differs by 10 %; the results should be comparable considering a large uncertainty of these estimations.

² calculated as 8 NOK = 1 €

Table 3–5 Cost estimates for different studies on post-combustion CO₂ capture: CO₂ capture plant with combined heat and power plant (chp plant) for energy supply

	IEA Study [MacDonald, 2008]	GassTek Study [Hegerland, 2006]
	3,000 tpd clinker coal fired chp plant	≈ 3,300 tpd clinker gas fired chp plant
CO ₂ reduction	85 %	85 %
CAPEX (M €)	294	110
OPEX (€/t CO ₂)	107	30
CAPEX (M €)		
<i>mechanical equipment</i>		
deNO _x	4.6	1.0
deSO _x	22.5	6.4
CO ₂ capture	31.8	32.0
CO ₂ compression	7.8	27.8
chp plant	66.2	27.8
other	0.1	14.8
<i>design, erection, contingency</i>		
construction, design, erection	123.0	included above
contingency, fees	38.0	n/a
Sum	294.0	109.8

These figures show a great variability and uncertainty. Due to a lack of realized full-scale projects, and due to ongoing fundamental research and development, actual numbers may significantly vary from these estimations.

Certainly, a main reason for the big difference between the numbers is the conceptual formulation of each study. The IEA study calculates costs for a hypothetical state-of-the-art cement plant while the GassTek work focuses on a certain plant.

3.8 Potential equipment suppliers

There is a variety of equipment suppliers which are involved in pilot or demo trials or which have even built CO₂ capture plants in various industrial sectors. The following non-exhaustive list gives an overview about some relevant companies.

CANSOLV (Canada):

CANSOLV Technologies Inc. (CTI) provides gas absorption solutions, e.g. for SO₂ and CO₂ reduction. In December 2008, Shell acquired 100% of the CANSOLV shares. The CANSOLV[®] CO₂ capture system is a regenerable carbon dioxide scrubbing process. This patented technology uses an aqueous amine solution, CANSOLV Absorbent, to achieve bulk removal of carbon dioxide from a large variety of gas streams [Sarlis, 2008].

Linde (Germany):

Linde-KCA-Dresden GmbH is a subsidiary of The Linde Group. As an engineering company for chemical and biotechnological plants, Linde-KCA has a long standing expertise in the CO₂ scrubbing of gases (the RECTISOL[®] process is a Linde technology) and the processing of CO₂, including its purification, compression and liquefaction. Linde is a supplier and a prospective partner for the building of plants for the capture and removal of CO₂ for the energy sector as well as for the chemical and metallurgical industry. Linde is also involved in several CCS projects, e.g. with Vattenfall (Schwarze Pumpe and Jämschwalde), RWE (Niederaußem), Gaz de France (Maxdorf) and Statoil (Hammerfest).

Fluor (USA):

Fluor is a plant supplier for carbon dioxide capture. Fluor uses different solvents like diglycolamine (DGA, Econamine) and MEA (Econamine FG). The Econamine FG Plus process is an energy efficient process for the removal of CO₂ from low-pressure, oxygen-containing flue gas streams. The solvent formulation is designed to recover CO₂ from low oxygen-containing streams that are at near-atmospheric pressure, such as burner flue gas streams [Reddy, 2008].

ALSTOM (France):

Alstom is company in the field of power generation and environmental technologies. The company designs, manufactures and supplies systems to the power generation industry - for gas, coal, wind, hydro and nuclear power - and industrial markets. Furthermore, Alstom offers technologies for CO₂ capture, focussing on oxyfuel combustion and post combustion capture. These technologies can be retrofitted to the installed base - an essential component to meeting future emission targets [Freeman, 2008].

Alstom is also working on a new post-combustion process involving chilled ammonia. This technology potentially has lower energy requirements, significantly reducing the cost of CO₂ capture. Alstom has announced partnerships with EPRI, Statoil, WE Energies, AEP and Eon in order to validate the process on an industrial level before the end of 2011.

Mitsubishi Heavy Industries (Japan):

Mitsubishi Heavy Industries (MHI) is a comprehensive manufacturer of machinery. MHI also offers large-scale plants for CO₂ recovery from flue gas. The MHI CO₂ recovery process utilizes "KS-1," an advanced hindered amine solvent, in conjunction with a line of special proprietary equipment. The technology was developed through cooperation between MHI and Kansai Electric Power Company, Inc. (KEPCO) [Kishimoto, 2008].

Mitsubishi Heavy Industries, Ltd. (MHI) and E.ON Energie AG will jointly test technology for recovering carbon dioxide from flue-gas emissions from a coal-fired power generation plant in Germany. The CO₂ recovery test will be capable of capturing 100 metric tons of CO₂ per day (flue-gas flow rate: 20,000 cubic meters per hour). The recovery plant operation will commence early in 2010. The various tests to be conducted at the plant will focus mainly on further reducing the amount of energy consumed to complete the CO₂ recovery process

Mitsubishi Heavy Industries, Ltd. (MHI) has signed a contract to carry out the technical pre-studies for the planned carbon dioxide capture plant in Norway from Gassnova SF in Norway. The planned facility will capture approximately 3,000 tons of CO₂ from flue gas emitted from an existing 420 MW gas fired power generation plant in Kårstø, which is located on Norway's southwest coast.

Tecno Project Industriale (Italy):

The Italian company "Tecno Project Industriale" (TPI) is a specialist company for the optimized treatment of industrial gases, focussing on the business areas of CO₂ production plants and CO₂ recovery plants. TPI built the post-combustion pilot plant at the Esbjerg Power Plant, which was used for the trials in the framework of the European CASTOR Project and which is currently being used for the trials in the framework of the CESAR Project.

3.9 Update on membrane technologies

Today membranes can be used for numerous applications. In the field of gas treatment they are employed for the recovery of methane from biogas, for the separation of air into N₂ and O₂, for the separation of CO₂ or H₂ from methane and other hydrocarbons. Furthermore membranes are subject of current research about CO₂ capture.

Gas separation membranes are thin barriers that allow selective permeation of certain gases. They are predominately based on polymeric materials. In most cases they are usually formed as hollow fibres arranged in the tube-and-shell configuration, or as flat sheets, which are typically packaged as spiral-wound modules.

One of the main advantages of gas separation membranes is that no regeneration is required - CO₂ capture can be achieved in one step. The systems are compact and lightweight, and can be positioned either horizontally or vertically, which is especially suitable for retro-fitting applications. The modular design allows optimization of process arrangement by using multi-stage operation, and low maintenance is required because there are no moving parts in the membrane unit.

A number of solid polymer membranes are commercially available for the separation of CO₂ from gas streams, primarily for natural gas sweetening. The driving force for the separation is

a pressure difference across the membrane. As such, compression is required for the feed gas in order to provide the driving force for permeation. In addition, the separated CO₂ is at low pressure and needs additional compression to meet pipeline pressure requirements. The energy demand for gas compression is significant when a very high pressure is required.

Investigations on laboratory level showed, that membranes can provide significant improvements compared to amine scrubbing technologies, especially with regard to the energy consumption. However, these results are only valid under certain circumstances, e.g. the flue gas composition, the permeate composition and the achievable recovery ratio [Bounaceur, 2006].

Furthermore a significant improvement is possible when membranes with tailor-made cavities are produced. This can be achieved by using various template molecules and heat treatments. According to the author the new membrane materials are 500 times more efficient than traditional membranes for CO₂ separation [Cho, 2007].

A new development is to operate the membranes under vacuum conditions [Ho, 2008]. In this case, the flue gas is pressurized to 1.5 bar, whereas the permeate stream is at 0.08 bar. The capture costs were calculated at \$ 54/t CO₂ avoided, compared to \$ 82/t CO₂ avoided for a pressurized feed. According to the authors a further reduction of the capture costs to less than \$25/t CO₂ avoided could be achieved, if membranes with improved permeability and selectivity are developed.

Special types of gas separation membranes are membrane absorbers, which are used to intensify absorption processes with well-known solvents (e.g. amines). Whereas gas permeation takes advantage of the differences in permeation rate through a polymeric or mineral membrane, membrane contactors (or membrane absorbers) make use of a microporous membrane which improves gas liquid interfacial contact. However, the technology has not been proven at a large scale. Therefore a pilot plant with membrane contactors at a coal fired power station is in planning stage [Meulemann, 2007]. A disadvantage of those membrane absorbers is that plugging can occur when impurities are in the gas stream. However, the advantages lie in the fact that the equipment can be made more compact and with a smaller footprint compared to standard amine scrubbing technology.

All in all the development of the last two years has shown that membrane technologies are not available for potential CCS pilot or demo projects. If the membrane characteristics could be improved and the costs of the (polymer) material could be reduced, membranes could become an interesting alternative to more developed post-combustion technologies in the long run – at least for small- and medium-scale installations.

4 Oxyfuel Technology

4.1 General Update on oxyfuel

The oxyfuel technology relies on pure oxygen instead of ambient air for combustion, i.e. the nitrogen is removed in a separation plant (ASU) from the air prior to being applied to the kiln. Consequently the concentration of carbon dioxide in flue gas is increased significantly. This will have a huge impact on the clinker burning process, mainly on the energy balance as well as the ratio between the enthalpy flow of the kiln gas and the energy needed for the chemical / mineralogical reactions of the kiln feed. The theoretic 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. Thus, the recirculation rate adjusts the combustion temperature. **Figure 4-1** shows the oxyfuel process with recirculating flue gas.

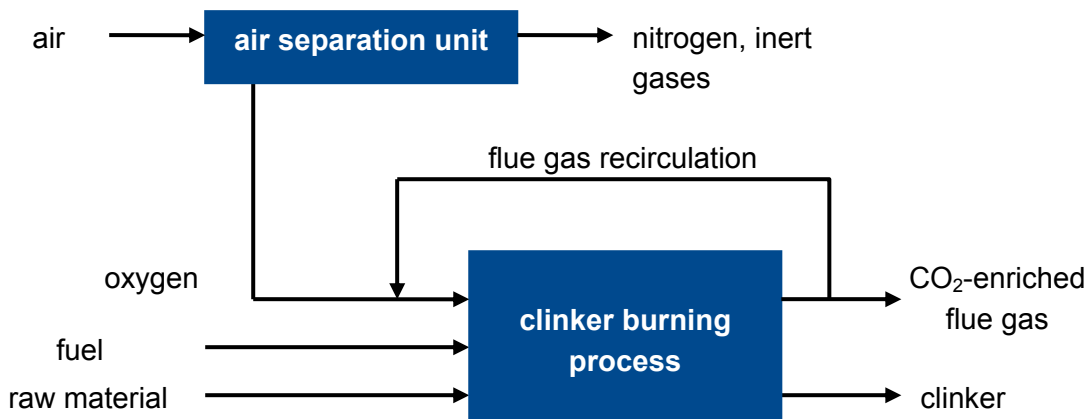


Figure 4–1 Oxyfuel technology with flue gas recirculation

From differences in gas properties (e.g. specific heat capacity, molar weights) of nitrogen compared to carbon dioxide results a longer and unstable flame as well as decreasing gas velocities at the same ratio of N_2/O_2 and CO_2/O_2 comparatively. Moreover the radiant heat transfer gains in significance due to the increasing emission ratio with increasing CO_2 concentration in the combustion gas. The oxygen concentration in the oxidizer therefore becomes an additional degree of freedom, whereas the optimum level will be higher than 21 vol.-%. In the energy sector an optimum oxygen concentration of 27 to 35 vol.-% has been reported with regard to the combustion characteristic compared to the air-based combustion. Ignition and burnout of fuels are positively influenced by the higher oxygen availability.

The advantage of pure-oxygen-based combustion is that the flue gas has a carbon dioxide concentration of around 80 vol.-%, compared to 14 - 33 vol.-% CO_2 for ambient-air-based combustion. Consequently, for CO_2 capture only a comparatively simple carbon dioxide purification is required. The remaining part of the flue gas comprises water steam from combustion, surplus oxygen and impurities of nitrogen and sulphur oxides. Dehumidification by condensation and technology for $DeNO_x$ and $DeSO_x$ are well-known and widespread. The oxygen and carbon dioxide recycle combustion process has also a further benefit in suppressing nitrogen oxide formation, lowering abatement costs for the removal of nitrogen

oxides. Nitrogen oxide generation is decreased, because nitrogen oxide exclusively originates from fuel-based nitrogen and nitrogen from false air, which also affects the oxygen concentration. Furthermore, nitrogen oxide is reduced by recirculating the flue gas.

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. Due to the fact, that the final specifications for the purity requirements are still being discussed in the scientific and regulatory community, the effort of the CO₂ purification can only be estimated nowadays. Some sulphur compounds and some other impurities would remain in carbon dioxide fed to storage, which may be acceptable in some circumstances.

4.2 State of the art

4.2.1 Oxyfuel technology in other industry sectors

The oxy-combustion has been pursued for example in the power generation, glass and steel sector for a longer time. That way larger scale applications of oxy-combustion have been seen in use in glass and steel melting furnaces focussing on increasing efficiency of the burning process. The application of the oxyfuel technology with flue gas recirculation for CO₂-emission reduction was investigated predominantly by the energy sector during the last years. After demonstrating the oxyfuel operation in small scale test rigs, the Swedish power company Vattenfall Europe built the first pilot plant with oxyfuel technology for power generation at the location Schwarze Pumpe, Germany, which started the large-scale test phase in 2008. The plant consists of a single 30MW_{th} burner and a subsequent flue gas cleaning. A cryogenic air separation plant for supplying oxygen with a minimum purity of 99.5 % and a CO₂ separation plant were installed onsite. After successfully proving the functionality of the Oxyfuel technology and the interdependency of burning process and chemical plants, the further work focuses on optimization and identification of critical points in up-scale. Moreover Vattenfall plans to bring two demonstration plants into service until 2015.

Furthermore one boiler of the power station in Callide, Australia is being retrofitted for oxyfuel combustion. Its advantage is the proximity to a geological area, where the liquefied gas can be stored in depleted natural gas fields. The start-up of the demonstration plant is expected in 2011. In addition Total reported of starting up a 30 MW gas-fired boiler, which they retrofitted with oxyfuel technology, in Lacq, France in the middle of 2009. The horizon of commercial implementation of oxyfuel technology is estimated to be around the year 2020 [Strömberg, 2008], [CCSD, 2008].

4.2.2 Oxyfuel technology in the cement industry

Although 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 on the plant operation. In the clinker burning process the oxyfuel technology with flue gas recirculation has not only an important impact on plant operation but also on product quality. The high partial pressure of carbon dioxide certainly affects the calcination, the reaction of calcium carbonate to calcium oxide and carbon dioxide. Also, unlike in steam boilers combustion in rotary kiln includes flames, which are non-premixed open jet flames. Consequently, research

and experience from boilers are not applicable to rotary kilns. Also flue gas enthalpy and streams are completely different to current cement plants.

Currently there are three projects reported to implement oxyfuel technology in the clinker burning process or other process firing systems:

- 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 the oxyfuel technology and comprises a cost estimation. A detailed configuration of an oxyfuel cement plant (compare **chapter 4.2.3**) was considered, whereas potential impacts on the process, including temperature profiles and material conversion were neglected.
- F. Zeman and K. Lackner from the Earth Institute at Columbia University reported in “A Reduced Emission Oxygen Kiln” about the impacts of oxyfuel combustion on the clinker burning process in 2008.
- The Research Institute of the Cement Industry is undertaking a project on the applicability of oxyfuel technology since 2007. The main research objectives are besides plant and process requirements and limits for oxyfuel technique, impacts on energy balance of process, clinker quality and plant operation as well as the identification of flue gas composition.

As reported these theoretical studies have not been followed by any larger-scale tests so far, due to some technical issues not being solved.

More experience is available for oxygen enrichment technology in rotary kilns for cement production especially from the US. There, the focus was not on further increasing the energy efficiency of the clinker burning process and reduction of the specific CO₂ emissions. The major objective was an increase of production capacity. New trials, e.g. in German cement plants were carried out aiming at increasing the use of low calorific value or secondary fuels. Although oxygen enrichment has not been applied with the aim to capture carbon dioxide, these experiments offer information about the application of oxygen in the burning process. By the use of additional oxygen the nitrogen fraction of the combustion gas is decreased, which has to be heated up in the case of combustion with ambient air. Therefore the adiabatic flame temperature rises and the flame becomes shorter and brighter. The oxygen boosted kiln combustion leads to ‘high value’ energy due to reduced nitrogen content which does not have to be heated up [Leger, 2001]. This energy can be used for the calcination and sintering process which results in a reduced gas volume or a rise of kiln capacity. That way an increase of 25 % to 50 % (short term experiments) of kiln capacity by an enrichment of 30 to 35 vol.-% oxygen in average has been reported. Other experiences show that under certain conditions oxygen enrichment is limited to an oxygen concentration of 23 to 25% in the combustion air [Gotro, 2001], [Shafer, 2001], [Manias,2001].

The measure is limited by increasing damages of the refractory in the sintering zone of the cement kiln and higher NO_x emissions due to increasing thermal NO_x formation. As the secondary air flow is reduced the heat recuperation in the clinker cooler might be affected for example by a higher secondary air temperature as well [Mayes, 2001]. In contrast other experiments with oxygen enrichment showed a positive impact on the refractory and kiln operation due a higher stability of the burning conditions [Mushulovic, 2002].

Oxygen enrichment has not been applied to reduce CO₂ emissions so far. But the use of enriched combustion air may result in fuel savings and thereby avoids CO₂ production. The decision for a dedicated oxygen supply system (on-site/off-site) depends on the specific need of the cement plant. But providing oxygen enriched combustion air induces energy penalties linked first of all to the oxygen production itself. Oxygen production needs comparatively high additional power consumption. Therefore the integration of the additional plant components plays an important role for the overall efficiency.

4.2.3 Integration of oxyfuel combustion into the plant technology

To integrate the oxyfuel technology into the clinker burning process additional plant components have to be complemented. An essential part for the oxyfuel combustion with CO₂ segregation constitutes the oxygen supply by an air separation unit and the CO₂ purification and compression facility, which are state-of-the-art. Both of these plant components are power intensive processes and consequently influence the energy consumption of an oxyfuel cement plant significantly. The increasing energy demand raises the question of energetic integration of these components in the burning process. As an approach to this issue a waste heat recovery boiler for electricity power production from flue gas energy is considered. In the following different technologies of these plant components and their influencing parameters on the energy consumption of the whole system are presented.

4.2.3.1 Oxygen Supply

Depending on production capacity, oxidizer purity, separation technology and oxygen pressure the commercially used air separation processes require between 0.25 and 1 MWh/t O₂. Basically the oxidizer is produced by the separation of air. Air consists mainly of nitrogen, oxygen, argon and small amounts of carbon dioxide. The different separation technologies are based on differences in boiling points, in molecular weights or other properties of the components. These are the cryogenic distillation and non-cryogenic methods, which are using membranes or adsorbents to remove the unwanted components. The range of purity, capacity and power consumption of the different separation systems are shown in **Table 4-1**.

Table 4-1 Application areas and power consumption of the oxygen supply systems

Separation system	oxygen purity [vol.-%]	capacity [t O ₂ /d]	power consumption [kWh/t O ₂]
Cryogenic air separation	< 99.9	< 5,000	220 - 400
Adsorption technology			
PSA	90 - 95	< 200	560 – 980
VPSA	90 - 94	< 250	300 – 420
Membrane system	< 99	< 35	~ 225
ITM, OTM			

As can be seen from the table the cryogenic oxygen production is currently the most power efficient technology for the production of large quantities of oxygen. Therefore the cryogenic technology is well-known and widespread. The system relies on different boiling points and can separate the air into its elemental components in liquid form at temperatures about -185°C . Beside oxygen production high-purity nitrogen and argon can be produced as by-products at relatively low additional costs. However the argon recovery is uneconomic unless the required oxygen is produced with purity higher than 97 vol.-%. The cryogenic technology uses multi-column cryogenic distillation to produce oxygen from compressed air. All cryogenic ASU devices consist of similar steps, which are illustrated in a general flow diagram in **Figure 4-2**. Every plant includes compression machinery, heat exchanger, distillation technology (“cold box”) and gas expander. After the initial compression of the incoming air carbon dioxide and the remaining water vapour, which has not been condensed during compression, are removed. Otherwise these components would freeze and cause deposit on the surface within the process equipment at the very low temperatures. For purification two basic possibilities exist: the molecular sieve and reversing exchangers. While the sieves remove the impurities by adsorption, the exchanger makes them freeze out on the walls. Subsequent the air feed is cooled down to -185°C by heat transfer with the cold product and waste gas streams. This minimizes the effort for an supplemental refrigeration process that includes expansion of additional pressurized air. The air feed is distilled into the elemental streams by a system, which includes a high and low pressure column. Nitrogen is removed in the high pressure part and is released at the top, whereas argon has a boiling point similar to that of oxygen and will preferably stay with the product. If high purity oxygen is required more distillation stages and a removal of argon from a point in the lower pressure column, where its concentration is highest, are necessary.

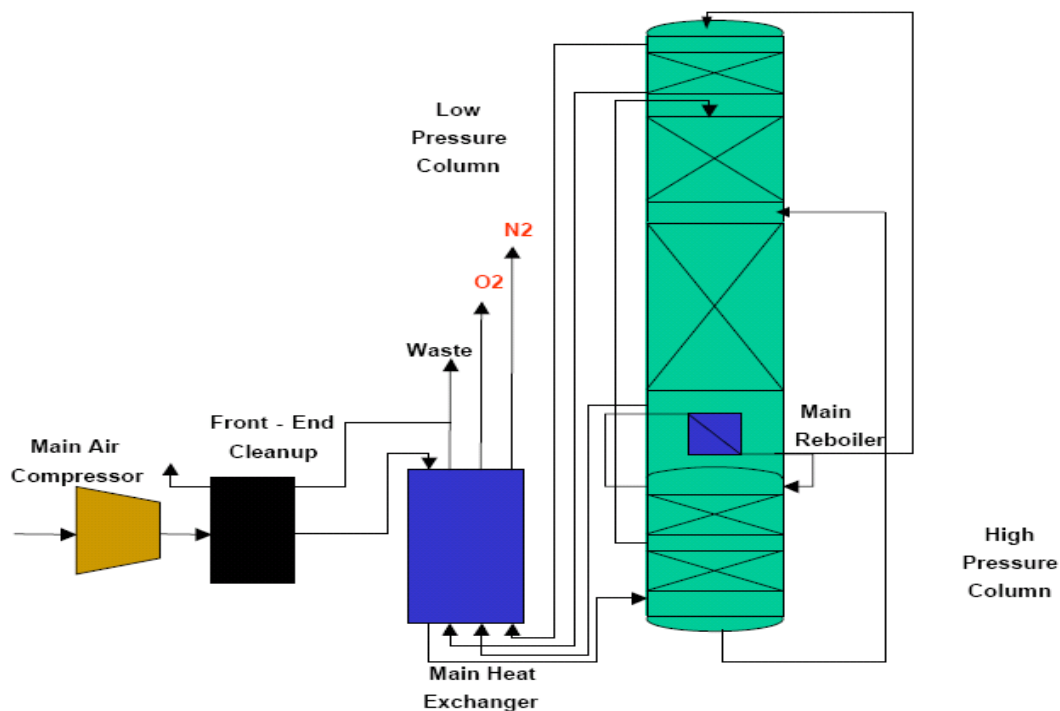


Figure 4–2: Flow diagram of a cryogenic air separation unit [Air Products]

The cryogenic air separation achieves inherently a high degree of efficiency, thus it becomes difficult to integrate the ASU energetically in the clinker burning process. Generally the oxygen can be produced by the cryogenic separation with purities up to 99.9 vol.-%, which significantly increases the energy demand. **Figure 4-3** illustrates the relative energy consumption for a distillation system as a function of oxygen purity. The separation efficiency rises until 97.5 vol.-%, where the curve shows a peak. While the relative energy is nearly constant in the range from 90 to that point, it increases significantly above 97.5 vol.-%. This represents a crossover point where oxygen-nitrogen separation transitions to oxygen-argon separation [Shah, 2002]. As the differences in boiling points of oxygen and argon are small, the power consumption rises. Although the higher oxygen purity enhances the subsequent CO₂ purification, the operating as well as capital costs of the ASU are substantially increased. Therefore the optimum purity is between 95 and 97.5 vol.-%.

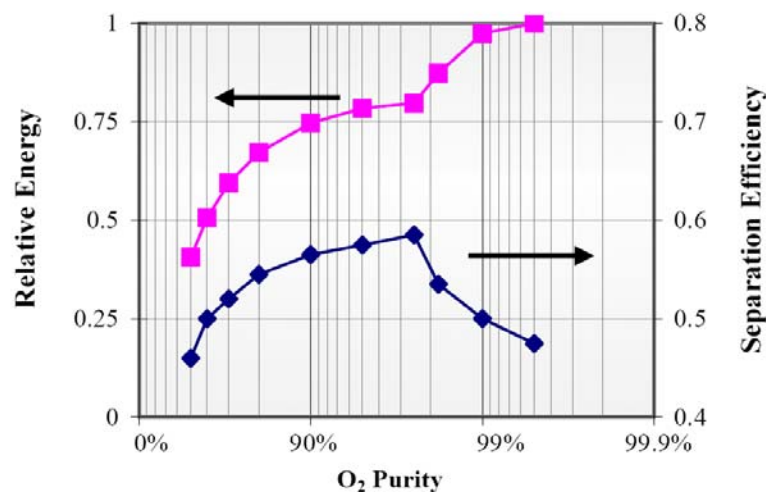


Figure 4-3 Relative energy consumption for the distillation system as a function of oxygen purity [Shah, 2002]

Alternative systems are based on adsorption or membrane systems and are currently only applicable to smaller quantities of oxygen. The adsorption technology (PSA/VPSSA) is based on the ability of porous materials to adsorb nitrogen. Compressed air is passed through a vessel containing adsorbent material like a zeolite bed, which retains the nitrogen until saturation. Regeneration can be achieved by reducing the pressure in the bed, which reduces the equilibrium nitrogen holding capacity of the adsorbent. The waste gas is then released into the atmosphere. **Figure 4-4** illustrates this functional principle. As the adsorbent bed requires periodic regeneration, the process operates batch-wise. Therefore the system usually consists of two vessels to provide continuous operation by cycling each bed sequentially from adsorption to desorption.

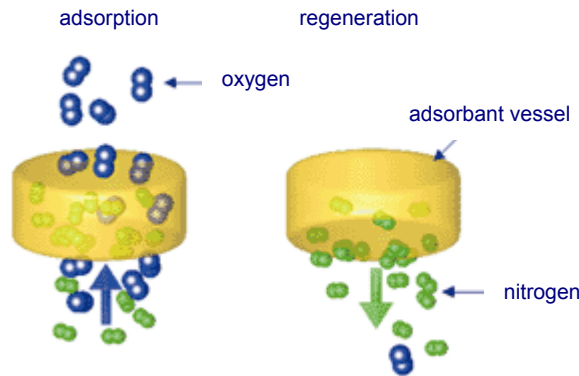


Figure 4–4: Functional principal of adsorptive separation systems [Air Liquide]

The different types of the process vary in the way to reduce the desorption pressure. While the Pressure Swing Adsorption (PSA) technology depressurizes compressed air to ambient pressure, the Vacuum-Pressure Swing Adsorption (VPSA) technology regenerates the bed by vacuum. Although VPSA plants are more costly to build, they are the most cost effective production of lower-purity oxygen because of the higher energy efficiency compared to the PSA. Multiple beds allow pressure energy recovery during bed switching and can additionally advance the operating efficiency. As the production is proportional to bed volume, the bed size is the controlling factor of the capital costs. As a consequence the capital costs do not decrease with scale as it is the case with cryogenic plants [CCSD, 2006], [Uigi].

Gas separation membranes rely on differences in physical and chemical interactions between gases and membrane material. Membranes made of polymeric material use the differences in the molecular size and consequently in the diffusion rate of the gases through the membrane, which separates high and low pressure streams. To achieve the production capacity the membrane material, which is designed as fibres or sheets, are usually assembled into cylindrical modules as can be seen in **Figure 4-5**.

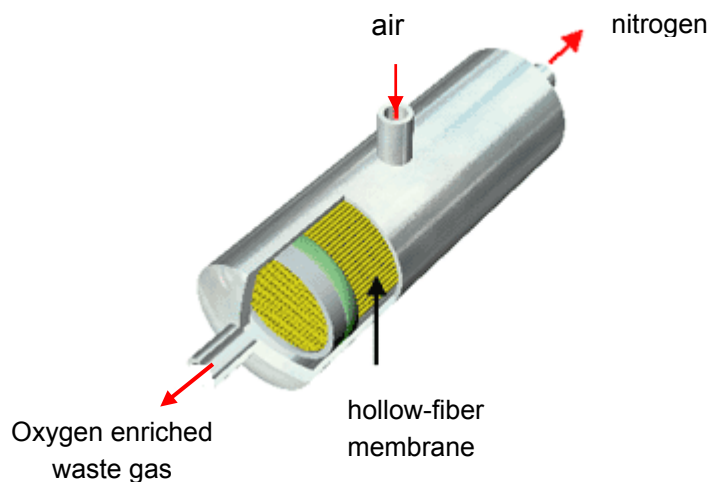


Figure 4–5: Section of a membrane diffusion separation system [Air Liquide]

The selectivity is a function of the permeability, which depends on the membrane type. Therefore they are especially suited to the production of oxygen enriched air with 25 to 50 vol.-%. As high concentrated carbon dioxide should be accumulated in oxyfuel operation, this process is infeasible due to the low oxygen purity. Nevertheless a main benefit of this membrane type is the simple and continuous construction at nearly ambient conditions.

Ion transport membranes (ITM) are made of solid inorganic ceramic materials, which permit a diffusion of oxygen ions (O^{2-}) through the ceramic crystal structure under the influence of an oxygen partial pressure or voltage gradient. This kind of membrane operates at high temperatures between 700 and 950°C. The differences in partial pressure or the electrical voltage will cause oxygen molecules to dissociate at the ceramic surface and pass into the crystal structure while on the permeate side of the membrane the oxygen ions give up their electrons and are recombined to oxygen. That way pure oxygen can be produced on the permeate side of the membrane. The operating principle of this process is shown in **Figure 4-6**. Currently membrane technology is a fast developing industrial branch. Selectivity, quality and throughput increases rapidly, whereas in comparison to cryogenic production of oxygen, it is expected, that air separation by membranes provides the cheaper solution, both in terms of capital and operating costs [Li, 2006], [TNO, 2006]. However, this technology is currently not robust enough for industrial application and does not provide large quantities of oxygen.

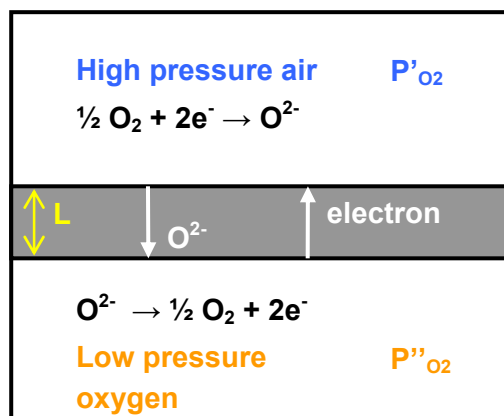


Figure 4–6: Functional principle of a ion transport membrane

4.2.3.2 CO₂ purification and compression facility

The compression of the flue gas is essential to enrich the CO₂ in the gas stream and provide the stream to the pipeline. The flue gas liquefaction or physical separation by compression-liquefaction is the most economic solution from today’s point of view. The disadvantage of this system constitutes a CO₂ containing exhaust gas stream to the environment resulting in a possible CO₂ capture rate of about 90 %. At higher requirements on purity a subsequent distillation after the liquefaction becomes necessary. The purity of the CO₂ is defined by the number of equilibrium stages in the distillation column. However this additional step has an adverse effect on the energy demand and system cost.

The final pressure (15 to 200 bar) of the CO₂, which can be generated by multi-stage compressors, is directly dependent on the transport distance. Assuming an ideal case, meaning the flue gas composition is adequate for the transport and storage requirements,

the gas pressure theoretically should only be adjusted to pipeline level. The number of required compressor stages again depends on the final pressure as well as on energetic and constructive aspects. For pipeline pressures up to 100 bar 6 to 7 compressor stages should be sufficient [Klostermann, 2008].

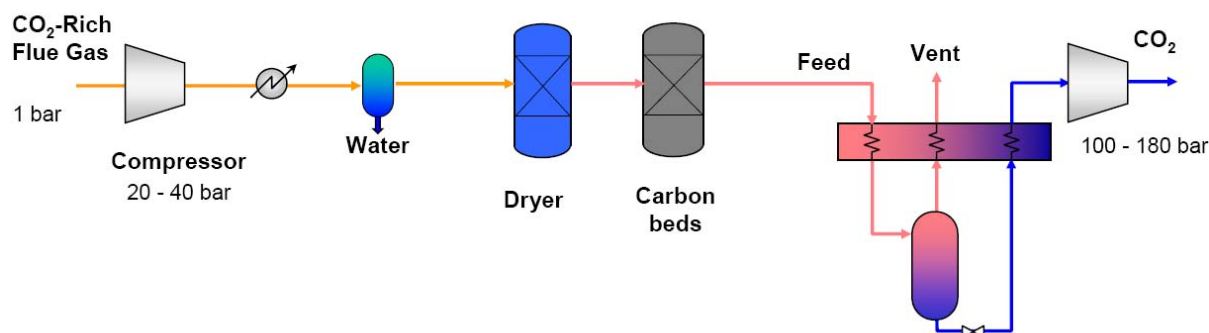


Figure 4-7: Flow diagram of a compression and purification facility [Shah, 2002]

In practice the flue gas comprises water vapor from combustion, oxygen, argon, nitrogen and impurities of nitrogen and sulphur oxides. This implies more or less complex gas purification steps. **Figure 4-7** shows a simple flow diagram of a commercial compression and purification facility.

In order to decrease the energy demand of the compressors the installation of intermediate coolers becomes reasonable. Simultaneously the remaining water can partially be removed as long as the critical point of the flue gas is not exceeded. In the condensate some CO₂ can be in solution, which partially emerges to the environment during the expansion. To avoid corrosion and plugging of the pipelines the gas should contain less than 10 ppm water vapour. Besides the formation of acids by the sulphur and nitrogen oxides, solid CO₂ hydrate can be generated from a physical combination of water and gas phase. Dehumidification by condensation and technology for DeNO_x and DeSO_x are well-known and widespread. If lower water contents are required an additional dehydration, which can use either liquid (i.e. glycols) or solid (i.e. silica gels, alumina, molecular sieves) desiccant for removing water, should become necessary. The selection of the appropriate desiccant depends on the requirements. While the liquids are generally more economically, they can not achieve the same level of dehydration like solids. Moreover carbon beds for removing impurities like heavy metal and Hg etc. may be installed [CCSD, 2006].

The CO₂ separation by liquefaction relies on the equilibrium distribution of the species between gas and liquid phase. The equilibrium phase diagram for pure CO₂ is shown in **Figure 4-8**. According to the pressure and temperature the equilibrium is shifted in the liquid region. Nevertheless the triple point limits the temperature because of the formation of carbon dioxide snow.

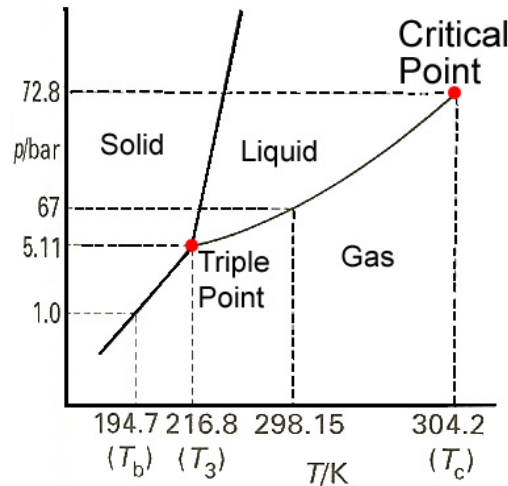


Figure 4–8: CO₂ phase diagram (vapour-liquid equilibrium)

By the presence of other gases the vapour-liquid equilibrium is affected. Aside from the CO₂ non-condensables (N₂, Ar, O₂, NO_x, SO_x) will be precipitated in the liquid. The higher the pressure at constant liquefaction temperature the higher is the fraction of highly volatile gases in the liquid phase. The separation ratio rises with higher pressure and lower temperature, thus the highest purity can be achieved near the limiting dew point. **Figure 4-9** illustrates the effect of non-condensables on liquefaction conditions for capturing 95 % CO₂ from flue gas. Thus it is evident, that the initial composition of the gas will determine the relative amounts of liquid and vapour under these conditions. At higher fractions of non-condensables higher pressures and lower temperatures are required, meaning the liquefaction effort rises. In addition, capture at these conditions will reduce the CO₂ purity.

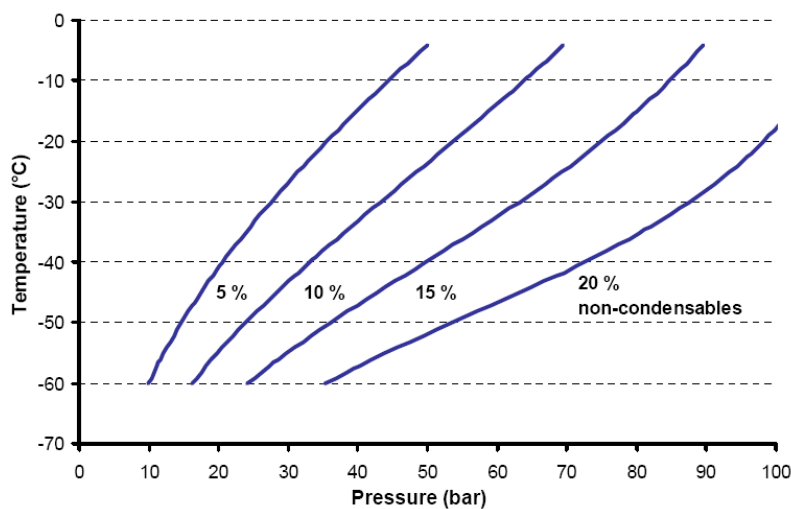


Figure 4–9: Effect of non-condensables on liquefaction conditions [CCSD, 2006]

In summary the dominating factors on the purification effort are false air, the molar ratio and the oxidizer purity. This circumstance results in a direct interdependency between the energy

demand of air separation unit and CO₂ purification facility. **Figure 4-10** demonstrates the dependency of specific energy demand from the fraction of false air as well as the used system (black curves: distillation, yellow curves: 1 stage compression) at an oxidizer purity of 95 % for an oxy-combustion boiler.

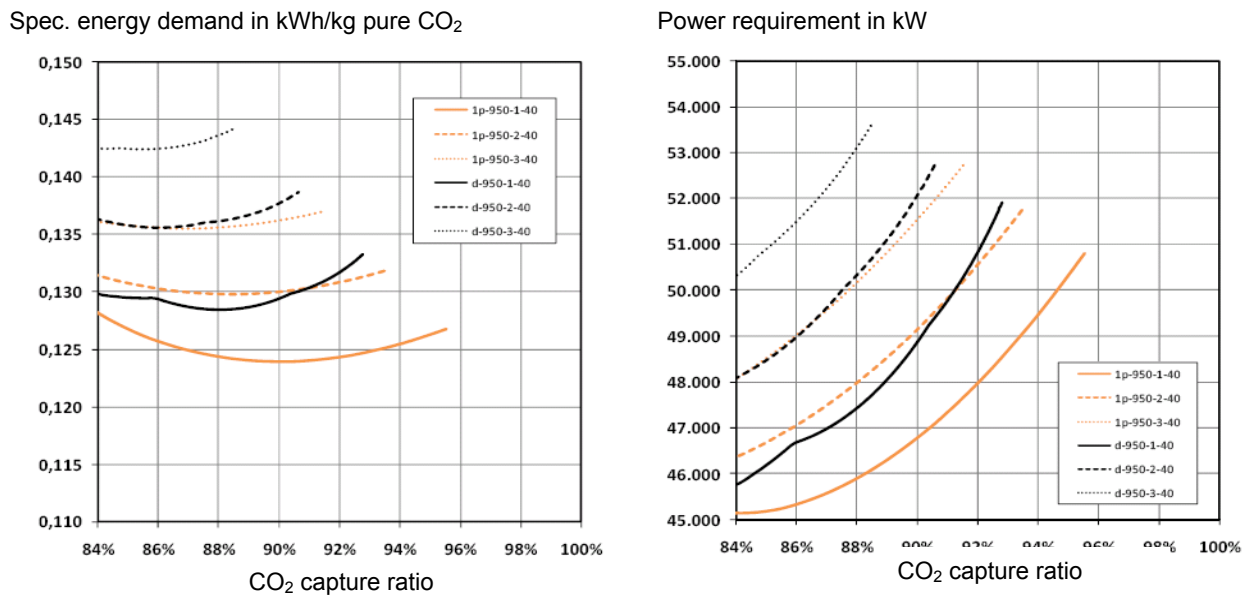


Figure 4-10 Energy demand for the CO₂ liquefaction [Klostermann, 2008]

The compression requires an energy consumption of 0.125 kWh/kg_{CO2} for only 1 % of false air and for the same capture ratio 0.136 kWh/kg_{CO2} at 3 % air leakage. Basically the specific energy demand increases by 4.5 % per percentage point of false air [Klostermann, 2008]. Likewise the energy demand is higher if a distillation system is used.

Another effect on energy consumption is the integration of cooling generation. The heat sink for condensation of CO₂ from flue gas can be produced by an external refrigeration process i.e. using NH₃ (0.13 – 0.14 kWh/kg_{CO2}) or internally by expansion of the waste gas flow as cooling medium itself (0.12 – 0.125 kWh/kg_{CO2}) [CCSD, 2006], [Klostermann, 2008], [Köpke, 2008].

4.2.3.3 Waste heat recovery

Waste heat from cement kilns, emitted by the raw and cooler exhaust gas, is usually used for drying raw materials like limestone, clay or marl. The required amount of heat energy strongly depends on the raw material moisture and therefore on the number of cyclone stages. At adequate energy level of the waste gas power can be generated from the waste heat based on the steam, the ORC (Organic Rankine Cycle) or the KALINA process, which require a heat recovery boiler and a turbine system. Although the steam turbine is the best-known technology, the relatively low temperature level of waste heat in cement plants (200 – 400°C) limits the efficiency to a maximum of 20 to 25 %. The ORC and KALINA technologies use organic substances or NH₃ as cycling media, which evaporate at lower temperatures and can therefore produce electric power at a temperature level at which steam turbines can not

work efficiently. By using those systems 8 to 10 kWh/t_{clinker} electrical power can be produced from cooler waste air and 9 to 12 kWh/t_{clinker} from the kiln gases, meaning in total between 7 and 22 kWh/t_{clinker}. If kiln operation is modified (e.g. less cyclone stages to increase raw gas temperatures) in order to produce more electricity, up to 30 kWh/t_{clinker} would be possible. This power generation can be further increased up to 45 kWh/t_{clinker} by additional co-firing into the boiler. This heat recovery offers the potential to generate approximately 50 % of the power required for the ASU. The technology is state-of-the-art in those regions of the world where public power supply is unsafe, e.g. some parts of Asia. [APP, 2008]

4.2.3.4 Overall layout for an oxyfuel cement plant

In the Technical Study published by IEA four possible configurations for an oxy-combustion cement plant were developed. Basically, in all cases the clinker cooler is excluded from the oxyfuel operation and thus is operated with ambient air. In the first configuration (**Figure 4-11**) both kiln and precalciner firing are supplied with oxygen (95 % O₂, 2 % N₂, 3 % Ar) from an air separation unit and therefore it is essential to reduce air in-leaks in these plant components. Thus the CO₂ generated in both preheater and kiln is captured. As mentioned the cooler is separated from the gas flow of the residual burning process. The cooler exhaust air is used for raw material drying. Nevertheless the heat achievable from cooler exhaust air could barely cover the required amount of heat for the raw material drying. On the other hand this offers the advantage of an air operated raw mill. That way air in-leaks into the mill are not relevant. The preheater exit gas is partially recycled. While one part is transferred to the CO₂ compression facility, the other one is recycled to the kiln. This poses the problem of thermal efficiency: In this configuration the recycled flue gas does not contain enough heat energy compared to the “normal” secondary air and therefore has to be heated up before entering the kiln. Furthermore the flue gas stream is used for fuel preparation (e.g. coal drying), of which heat requirement is lower than for raw material drying, and not fully utilized. Otherwise the mill can be operated with inert gas, but therefore shall be air in-leak free.

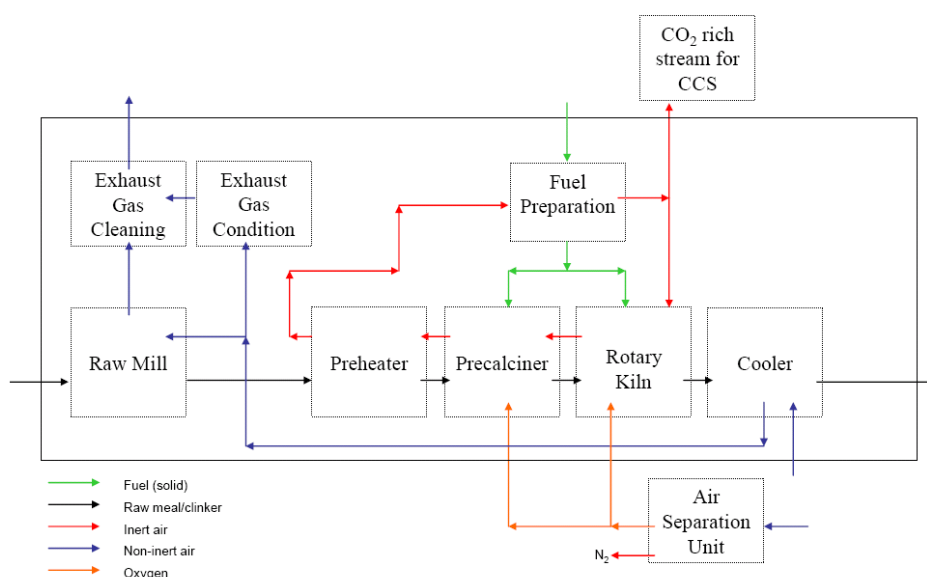


Figure 4–11 Oxy-Combustion Cement Plant Configuration 1 – diversion of preheater exit gases for fuel drying and subsequent capture or recycle [IEA, 2008]

Basically the second configuration (**Figure 4-12**) is similar to the first. The basic difference is that kiln gas is used for raw material drying and cooler waste air for fuel preparation. The heat demand of fuel preparation and raw material drying are better matched in this configuration. But in this case a non inert gas is used for fuel preparation, which might cause operational difficulties as it is a less safe mode of operation. The great issue in this case is - as in the previous case - a separated cooler and therefore the need of preheating the recycled flue gas. The third case is similar to configuration 2, but is operated with a “leak-free” raw mill, whose design would involve a significant effort and increasing costs. Nevertheless air in-leaks are not avoided in the preheater and kiln.

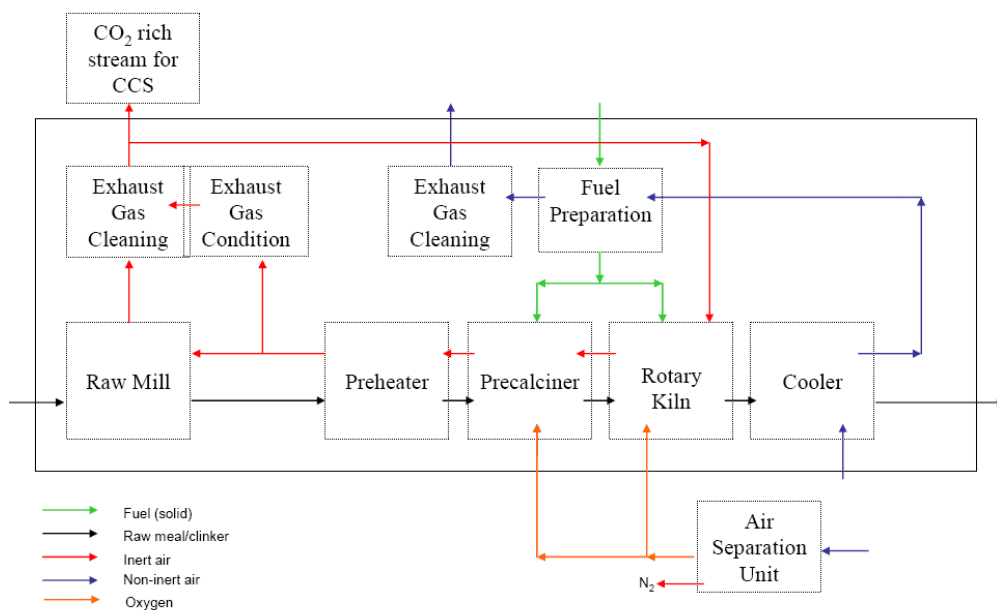


Figure 4-12 Oxy-combustion cement plant configuration 2 – capture and recycle of all Flue Gases from cement plant with diversion of cooler exhaust for fuel drying [IEA, 2008]

The last configuration (**Figure 4-13**) shows a dual preheater system with oxy-combustion in the precaliner only. This configuration has been chosen by the authors as the most promising one though only roughly 60 % of the CO₂ produced are abated. The flue gas from the precaliner is led into the preheater string 2, from which the gas is transmitted to the CO₂ compression facility and partially recirculated to the precaliner. The recycled stream is heated up to temperatures approaching the precaliner operation temperatures by the tertiary air from the cooler passing a gas-to-gas heat exchanger. The part of the flue gas, which is sent to the purification, is cooled by the oxygen stream from the air separation unit (ASU) to approx. 250°C. Before the CO₂ purification the gas stream is dedusted by an electrostatic precipitator (ESP). It was assumed, that an ESP operates better at that high temperatures than a bag filter. The oxyfuel operation only affects this particular plant component, where the majority of the CO₂ is generated due to combustion (of nearly 60 % of the fuel demand) and decarbonation of the raw material. By these means the cooler, kiln and one preheater string can be operated conventionally and less modifications of the plant components have to be made.

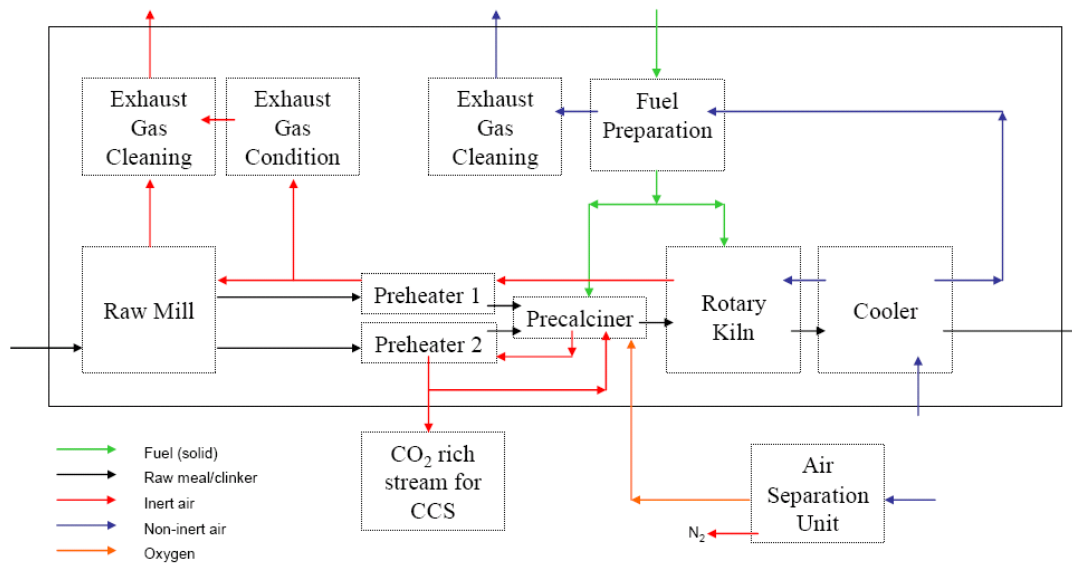


Figure 4–13 Oxy-combustion cement plant configuration 4 – dual preheaters with oxy-combustion in the precalciner only [IEA, 2008]

The raw material is dried by the raw gas stream from preheater string 1, which is conveyed from the kiln. Furthermore the fuel preparation is operated with the non inert cooler exhaust air. That way the difficulties with air in-leakage in the kiln and the raw mill are avoided. On the other hand more interfaces between the components due to the complexity of the configuration could also cause the problem of sealing. By the reason of affecting only a single part of the cement plant, the authors also considered a retrofitting of an existing plant with a twin preheater tower. However the ratio of gas flow and raw material flow could be disturbed due to the different material properties (e.g. density) of CO₂ and N₂. Hence it might be necessary to modify the oxyfuel preheater string. The disadvantage of this solution is that only a part of the generated CO₂ can be captured and approximately 38 % are still emitted.

4.3 Research activities within the ECRA project

Although a few cement plants use oxygen to increase throughput of kilns and enhance the energy efficiency, there is still very little experience with the impacts of oxyfuel operation on the clinker burning process. To proof the applicability of the oxyfuel technology for the cement industry research was started by ECRA, including laboratory tests and calculations with a process model. Besides these basic investigations more detailed specifications of an oxyfuel cement plant, like basic configurations and requirements on the flue gas conditioning, were elaborated in collaboration with industry partners from the cement industry, gas suppliers and plant manufacturers. Resulting from this discussion two possible configurations for retrofitting and new installations were chosen as most practicable with an acceptable energy efficiency. All investigations are based on the reference case presented in Appendix 10.1.

4.3.1 General layout

To design a general layout of an oxyfuel cement plant different configurations were considered. Therefore issues like the integration of raw material drying in the oxyfuel operation or cooler technology have been taken into account. The principal configuration of an oxyfuel cement plant, on which the current modelling of the clinker burning process is based, remains nearly unchanged to the conventional technology and is illustrated in **Figure 4-14**. A more detailed description of the burning process is given in Appendix 10.1.

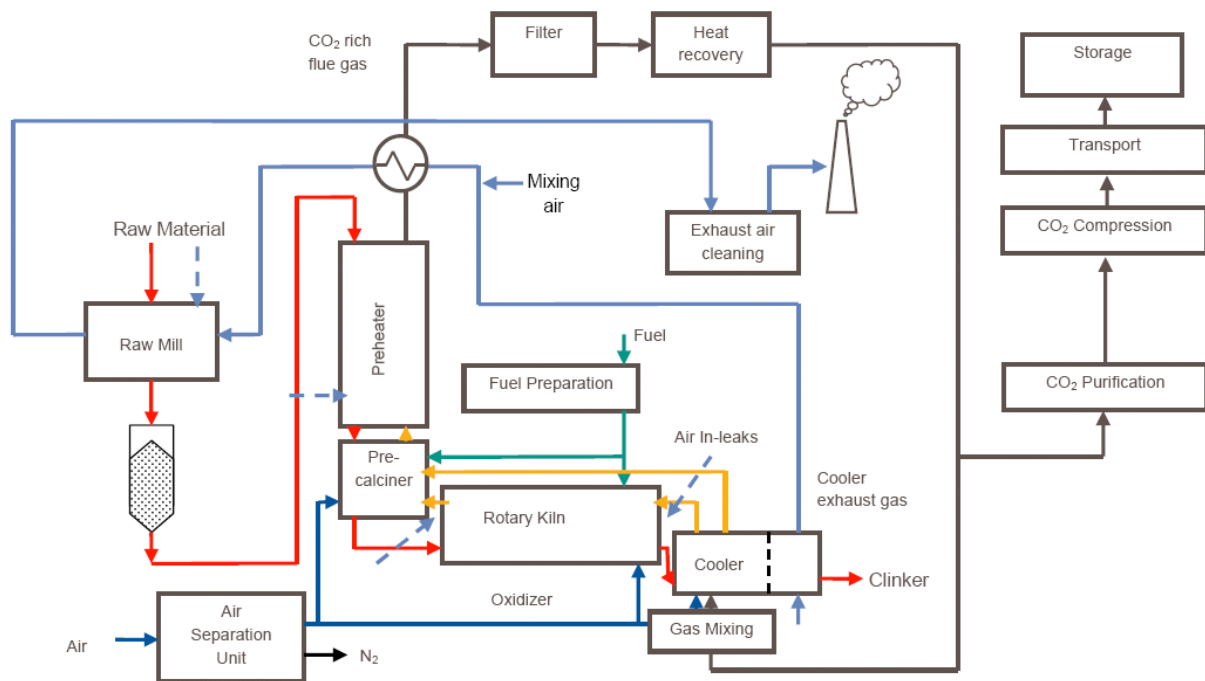


Figure 4-14 Investigated configuration of an oxyfuel cement plant

The basic geometry of rotary kiln, preheater tower and calciner is kept unchanged barring tighter sealings. The modifications in the configuration and plant specifications are discussed in the following.

Grate cooler

In contrast to the IEA study the grate cooler stays implicated in the gas flow, in order to avoid a separate preheating of the recycled flue gas. To prevent CO₂ emissions with the cooler waste 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 recirculated flue gas, which is needed in the burning process. As this would cause too high clinker temperatures a second cooler stage, which is operated with ambient air, is considered. This air leaves the cooler as exhaust air and can be used for raw material drying or fuel preparation. Generally two stage coolers are already in use for other applications in some cement plants.

Raw material drying

Waste heat emitted by the raw and cooler exhaust gas is usually used for drying raw materials. The integration of the raw meal drying and fuel preparation constitutes an issue in oxyfuel operation. Basically two different possibilities are conceivable, meaning the raw material drying via the recycled flue gas stream or cooler exhaust gas. In the first solution of raw material drying the air in-leakage in the raw mill has to be reduced as much as possible, which constitutes technical and economical problems. To avoid the necessity of an air tight raw mill the cooler exhaust gas, which consists of ambient air, is used for drying. On the other hand the exhaust air ($1.04 \text{ m}^3 \text{ STP/kg}_{\text{clinker}}$) leaves the cooler with a temperature of about 280°C , meaning that the energy content of the air ($269 \text{ kJ/kg}_{\text{clinker}}$) and the energy demand for drying might not match. In **Figure 4-15** the specific heat demand in $\text{kJ/kg}_{\text{clinker}}$ for drying cement raw materials in relation to the raw material moisture is shown.

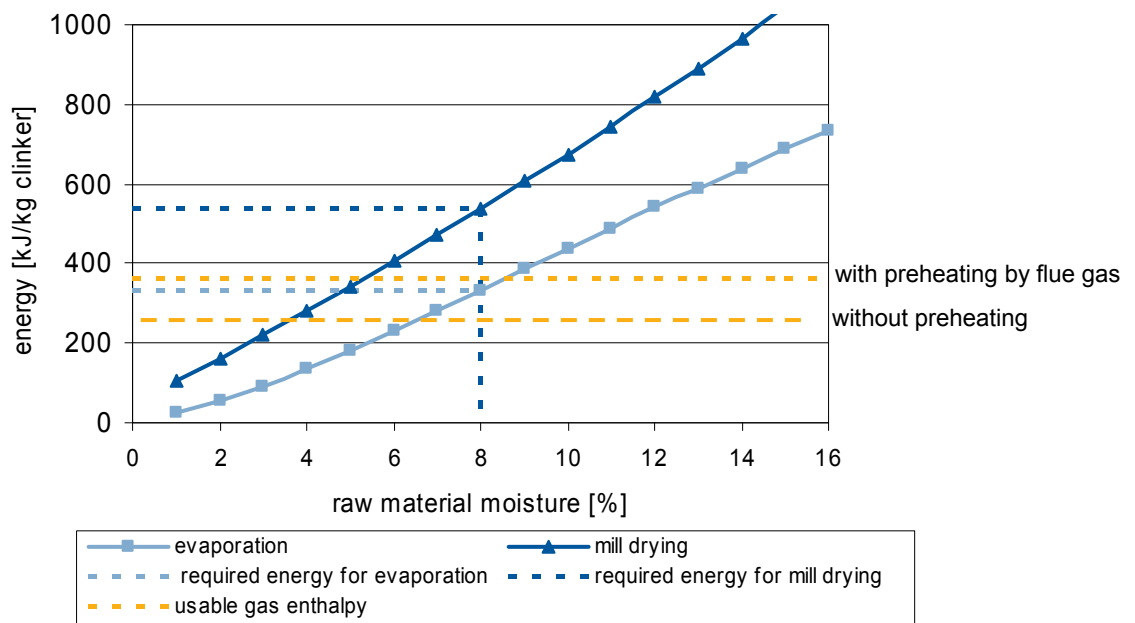


Figure 4-15: Required drying energy in relation to raw material moisture

Assuming an average raw material moisture of 8 % and a clinker production of 3,000 t/d the required heat energy for drying-grinding amounts to 538 $\text{kJ/kg}_{\text{clinker}}$. The yellow lines mark the usable gas enthalpies for drying at gas temperature above 100°C . As can be seen the gas heat energy does not match the drying without any additional heating. On the contrary the flue gas leaves the preheater with approx. 350°C ($639 \text{ kJ/kg}_{\text{clinker}}$). Adding a gas-to-gas heat exchanger the exhaust gas could be preheated up to 340°C by the flue gas. The usable energy rises to 375 $\text{kJ/kg}_{\text{clinker}}$, which could dry raw materials up to 5.5 % moisture. To further reduce the flue gas temperature and thus increase the ratio of recovered heat from flue gas additional ambient air could be added to the cooler exhaust air before entering the heat exchanger. Additionally the higher gas flow rate would benefit the drying in the mill. That way the flue gas temperature could be decreased to approx. 240°C via mixing exhaust gas and ambient air with the ratio 2:1. Whereas the recovered heat increases, the gas enthalpy

of drying gas decreases due to ambient air mixing. Nevertheless the energy demand of raw material moisture above 6 % cannot solely be matched via preheating with flue gas. The remaining energy of 160 kJ/kg clinker for 8 % moisture can be met by additional firing of fuel in the raw mill, which leads to unabated CO₂ emissions. A further approach to increase the drying gas enthalpy constitutes constructive arrangements of the kiln plant in order to increase the preheater exit gas temperature. (At higher raw material moistures this is conventionally used in some cement plants.) In this case it would be necessary to reduce the preheater cyclone stages to minimum 4 stages to adjust the required energy for 8 % moisture. As the additional firing of fuel would be shifted into the kiln, these CO₂ emissions could be captured.

Filter

As the flue gas can be cooled down by the gas-to-gas heat exchanger to 240°C before entering the subsequent filter, a conventional bag filter can be installed. The filter has to collect the dust to less than 10 mg/Nm³.

Waste heat recovery

The efficiency of waste heat recovery is limited by the flue gas temperature. Preferentially, the remaining flue gas enthalpy should be available for the raw material drying. Therefore the heat recovery operates more efficiently for lower raw material moisture, meaning higher remaining flue gas energy. By the use of the ORC or KALINA process the production of 12 kWh/t_{clinker} in average is achievable. Due to the requirement on continuous operation of these processes and thus on a continuous high energy content of the flue gas, their application tends to be appropriate at raw material moistures below 5 %. At high electricity prices the preheater exit gas temperature can be increased by modifying the kiln plant. That way power can be produced in order to cover a part of the power which is used for CO₂ compression at the expense of the kiln efficiency. Anyway the flue gas temperature should not be cooled to less than 120°C in order to avoid corrosion by the formation of acids.

Oxygen supply

An oxygen enriched stream (oxidizer) is provided to the precalciner and kiln firing (as primary "air") as well as to the premixing of cooling gas by a common air separation unit. For a medium-size cement plant with a kiln capacity of 3,000 tpd the oxygen demand is estimated to be around 50 to 55 tph. Such amounts of oxygen must be provided by an on-site oxygen supply system. Oxygen can be produced on the cement plant premises by several methods. The decision for a dedicated oxygen supply system must be based on an analysis of the specific needs of the cement plant in question. **Figure 4-16** shows the application areas of these systems depending on the production capacity and oxidizer purity. For very large usage a cryogenic air separation is the preferred choice. As mentioned in **chapter 4.2.3** the economic optimum of oxygen purity is found in the range between 95 and 97.5 vol.-%. Therefore the oxidizer composition is assumed as followed: 95 % oxygen, 1.5 % nitrogen and 3.5 % argon.

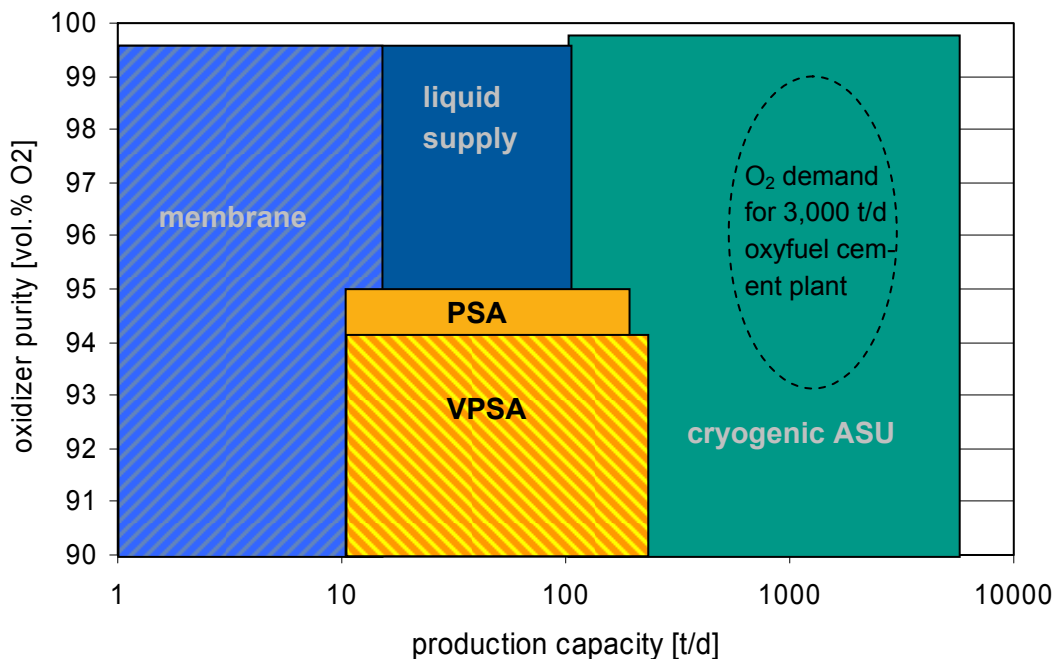


Figure 4-16 Application areas of different air separation systems

CO₂ purification and compression facility

After dedusting and cooling the flue gas is separated into a recycled part and a part for compression. As the requirements on CO₂ purity for sequestration remain still unclear, the concentrations of NO_x and SO_x are assumed to be limited to < 150 ppm and < 100 ppm. This may require an additional flue gas cleaning (SNCR/SCR and desulfurization).

The general mode of operation of an CO₂ liquefaction has been described in chapter 4.2.3. As mentioned before the required energy for the CO₂ capture strongly depends on the flue gas composition and the concentration of non-condensable components (nitrogen, oxygen and argon). The main factors, which affect the concentration, are false air in the plant and the oxidizer composition (oxygen purity). The effect of these factors is shown in **Figure 4-17** for an oxygen level of 21 vol.-% and an oxygen excess of 3.5 vol.-%.

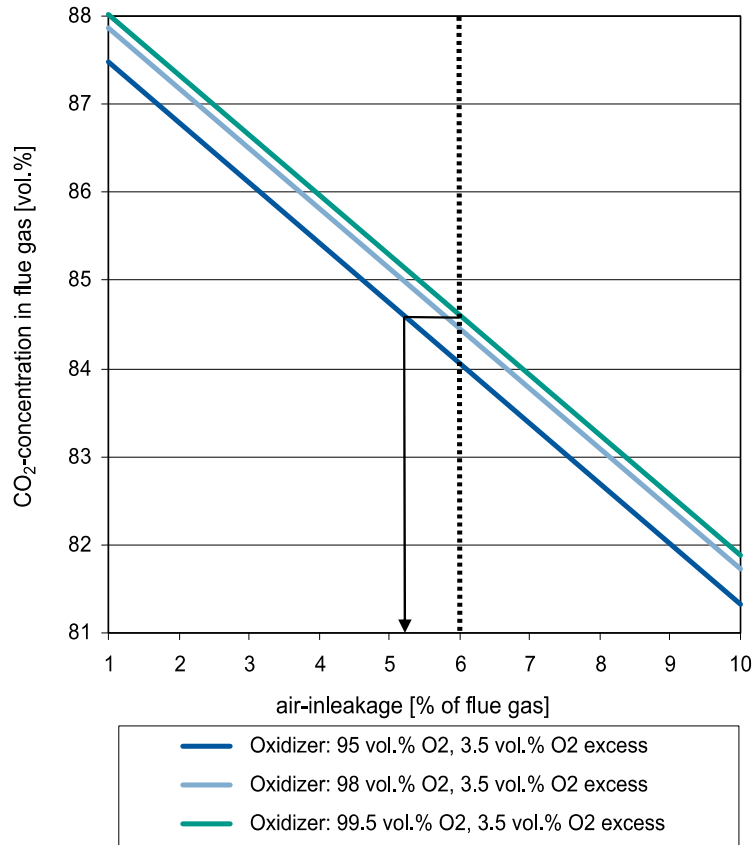


Figure 4-17 Effect of air-inleakage and oxidizer composition on the dry flue gas composition

Generally about 6 to 10 % of the flue gas from a commercial kiln plant consists of ambient air ingress due to the slight negative operating pressure. At an air ingress of 6 % nearly 84.5 vol.-% CO₂ can be achieved in the flue gas in the case of recirculation. It appears, that an increase of the oxidizer purity from 95 % up to 99.5 %, which is connected to a substantial increase in energy consumption and therefore operating costs, can be compensated by reducing false air by approx. one percentage point. Moreover the energy demand for CO₂ liquefaction rises by nearly 4.5 % per percentage of false air. Nevertheless false air, which infiltrates in the burning process, allocates oxygen for the combustion. Meaning at constant oxygen excess less oxidizer from the ASU has to be supplied. At the same time the flue gas flow increases due to the additional nitrogen fraction, which increases the flow for the purification. In contrary sealing the kiln would increase capital costs, but would probably be the more economic solution in the long term.

Complete sealing of a cement plant poses a challenge as a consequence of the connection between static and dynamic components, i.e. at the kiln inlet and hood, safety and economic aspects. Likewise a decrease of the oxygen purity in the oxidizer increases the argon and nitrogen fraction and therefore the oxidizer flow increases for the same oxygen level. Consequently the impurities in the flue gas flow rise. In summary the percentage of air ingress has the more distinct effect on the purification effort.

A short summary of the discussed specification is listed in **table 4-2**. In addition a comparison including the disadvantages (orange) and advantages (green) of the described solutions of the presented and the IEA configuration is given.

Table 4-2 Comparison of the configurations for retrofitting and new built plants

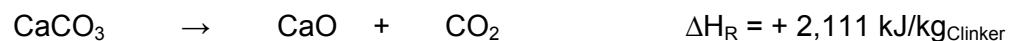
	IEA Configuration (Figure 4-13)	Ecra Configuration (Figure 4-14)
Captured CO ₂	Only CO ₂ generated in the precalciner (from decarbonation and fuel in precalciner firing)	CO ₂ generated in kiln, precalciner and preheater
Configuration		
Preheater	Twin preheater tower String 1: conventionally operating String 2: Oxyfuel operating	Preheater tower affected by the Oxyfuel operation
Precalciner	Oxy-combustion only in precalciner. Preheating of the recycled flue gas necessary (thermal efficiency)	Supplied with hot combustion gas from kiln and cooler
Kiln	Conventionally operating	Oxyfuel operation: Impacts on process and air in-leaks
Clinker Cooler	Conventionally operating	Two-stage Stage 1: CO ₂ /O ₂ mix Stage 2: Ambient air No additional preheating of flue gas
Raw material drying	Drying by combustion gas from preheater string 1 (conveyed by the kiln)	Drying by cooler exhaust air, which is preheated by preheater exit gas
Raw mill	Non affected	Non affected
Fuel preparation	Non-inert cooler exhaust gas	Separate (additional firing, but inert)
Flue gas recirculation/conditioning	Only the capture stream is conditioned	Both captured and recycled streams are conditioned
Cooler	Gas-to-gas heat exchanger from 330 to 248°C. Cooling medium: oxidizer from ASU (16°C)	Gas-to-gas heat exchanger from 350 to 240°C by drying gas. (Optional at low raw material moistures: heat recovery boiler to gain energy for compression)
Filter	ESP (hot gas) after cooler	Bag filter (<10 mg/Nm ³)
Preheating	Gas-to-gas heat exchanger from 325 to 775°C. Cooling medium: tertiary air from clinker cooler (795°C)	Preheating of combustion gas in the clinker cooler
Retrofitting	Possible, because of less modifications of plant components.	More appropriate for new installed cement plants

4.3.2 Impact of the oxyfuel combustion on the burning process

Due to the changing burning atmosphere ($\text{CO}_2/\text{O}_2/\text{N}_2$), the oxyfuel technology with flue gas recirculation has an important impact on both plant operation and mineralogical conversion of the kiln feed during the burning process. Therefore the research activities cover process modelling with the current kiln simulation scheme as well as laboratory tests with raw meal samples under different synthetic kiln atmospheres.

4.3.2.1 Impact on raw material decarbonation

The increasing CO_2 partial pressure caused by the Oxyfuel operation affects the chemical mineralogical material reactions, in particular the decarbonation reaction. The decomposition reaction of the limestone influences the energy demand of the burning process significantly due to its strong endothermic character.



Basically this is a heterogeneous reversible equilibrium reaction of dissociation and recarbonation, which proceeds depending on surrounding conditions until saturation within seconds. Thereby 44 % of the calcium carbonate mass is released as carbon dioxide. The difference of CO_2 equilibrium pressure and CO_2 partial pressure of the surrounding therefore constitutes the driving force of the reaction. More precisely, the reaction only occurs, if the equilibrium pressure, which is strongly depending on the temperature, exceeds the surrounding CO_2 partial pressure. This relation can be mathematically described for the system of pure calcium carbonate as follows:

$$p_{eq} = p_{eq,max} \cdot \exp\left(\frac{\Delta \tilde{h}_R}{\mathfrak{R} \cdot T}\right) \quad p_{eq,max}: 4 \cdot 10^7 \text{ bar and } \Delta \tilde{h}_R = 168,000 \text{ kJ/kmol}$$

While the qualitative coherence can be transferred to raw meals, the quantification of this relation for CO_2 partial pressures above 0.4 bar as it is the case in Oxyfuel operation has not been performed for clinker raw meals.

To quantify the impact of the increasing CO_2 partial pressure on the material reaction three raw meals from different origin and pure calcium carbonate were tested. **Table 4-3** shows the characterization of the tested materials. These materials were heated under predefined atmospheres in a laboratory kiln to obtain the degree of decarbonation of the samples via detecting the mass losses. CO_2 concentrations of 20, 40, 60, 80 up to 100 vol.-% in the atmosphere were tested, while the O_2 concentration varies between 0, 3 and 6 vol.-%.

Table 4–3 Characterization of the tested raw materials

Parameter	kiln meal 1	kiln meal 2	kiln meal 3
Geological origin	Shelly limestone	Shelly limestone	jurassic
CaO [wt.-%]	43.72	42.56	43.57
SiO ₂ [wt.-%]	13.70	12.95	15.21
Al ₂ O ₃ [wt.-%]	2.80	3.24	2.53
Fe ₂ O ₃ [wt.-%]	1.10	1.51	0.90
Lime standard	103	104	94
Alumina modulus	2.6	2.1	2.8
Silica modulus	3.5	2.7	4.4
Specific surface [cm ² /g]	4,250	5,450	5,740
Fraction of added Si-component (sand) [%]	8.9	4.6	0.0 (marl)

In order to consider all influences of the gas atmosphere on the decarbonation, first the influence of the oxygen concentration was examined. No significant influence of the oxygen content in the burning atmosphere turned out. For this reason the concentration was held constant at 3 vol.-%. Further laboratory tests confirmed a different shifting of the equilibrium of the calcination reaction to higher temperatures up to 80 K between the raw meals among each other and the calcium carbonate due to an increased CO₂ partial pressure. **Figure 4-18** exemplarily illustrates this issue for the decarbonation of kiln meal 2.

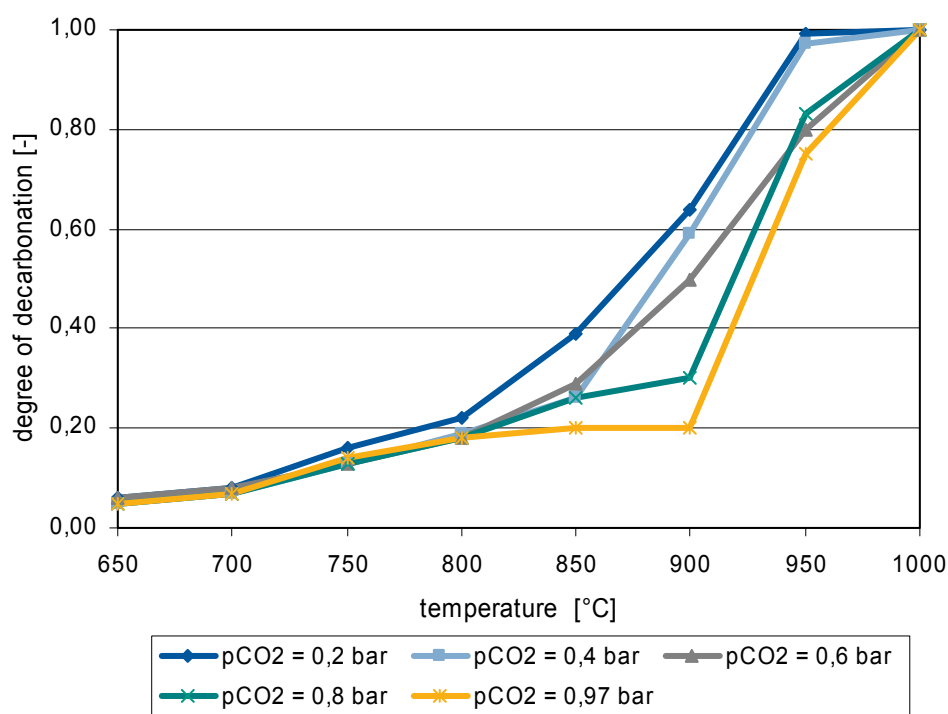


Figure 4–18 Equilibrium shifting of the decarbonation reaction of kiln meal 2

Furthermore the calcination of calcium carbonate was more influenced by the CO₂ partial pressure than the raw meals (compare **Figure 4-19**). These observations were discussed in detail. It was concluded, that the calcination reaction is mostly influenced by the subsequent exothermic clinker phase formation below 1,000°C due to the additional heat release. For this reason it was possible that the raw meals obtained higher degrees of decarbonation with same heat input than the pure calcium carbonate. To investigate the differences between the raw meals some characteristics (e.g. chemical composition, particle size distribution, specific surface area) were analyzed. These analyzes pointed out, that the sensitivity of the calcination reaction with regard to CO₂ partial pressure is basically affected by a closure level of silicon und calcium oxide constituents, which strongly affects the diffusion driven subsequent reactions.

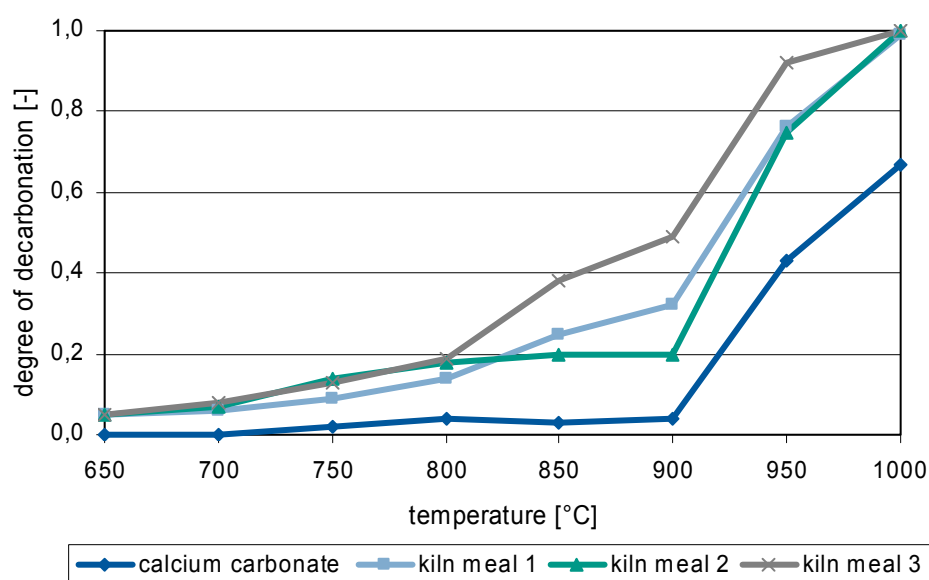


Figure 4-19 Comparison of the raw materials and pure calcium carbonate decarbonation shifting at a CO₂ partial pressure of 0.97 bar

Basically the laboratory tests showed an increase of the reaction enthalpy by 90 kJ/kg_{clinker} due to temperature shift of the decarbonation reaction. Apart from the higher energy consumption, the required higher temperature in the calciner may cause problems with the refractory and with burning low-calorific secondary fuels. Therefore the decarbonation reaction might partially be relocated into the kiln itself.

4.3.2.2 Modelling of the clinker burning process

To evaluate the impacts of an increased CO₂ partial pressure caused by the oxyfuel operation on the kiln operation a process engineering model, which has been developed by the Research Institute of the Cement Industry, was used. The model describes the process from the kiln feed to the discharge of the clinker from the cooler and is made up of individual

models for the plant components preheater, calciner, bypass, rotary kiln and grate cooler. Because of this modular structure the different plant configurations can be mathematically simulated. In addition the individual plant sections can be defined geometrically so that different plant sizes can be modeled. 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.

To quantify the impact of oxyfuel operation a reference case was defined. The starting point describes a so-called BAT (Best Available Techniques) reference plant with an energy consumption of 3,026 kJ/kg_{clinker} at a production capacity of 3,000 t/d. The plant consists of a rotary kiln with a 5-stage cyclone preheater, a calciner with tertiary air duct and a grate cooler.

However the calculations with the existing modelling scheme can not be accomplished without any limitation, thus following assumption were made:

- No modification of flame geometry and radiation
- Neglect of potential impacts of a changing gas composition on mineralogical conversion of the kiln feed
- An oxidizer purity of 95 vol.-% O₂, 3.5 vol.-% Ar and 1.5 vol.-% N₂ was assumed for the reasons described above(**chapter 4.3.1**)
- The grate cooler was abbreviated to simulate the first stage. The second stage with cooling by ambient air has not been modelled (yet) because it is not required for the Oxyfuel operation of the kiln itself.

Step 1: Substitution of primary air by pure oxygen

In the first step the nitrogen was removed from the primary air based on the reference case. Basically the simulations showed an increasing temperature profile in the kiln with increasing oxygen concentration in the primary air compared to the reference case due to the elimination of the nitrogen as inert gas. The sintering zone temperatures rise by 140 K in the gas and 50 K in the material. This may have negative effects of the kiln refractory. Nevertheless there were hardly no negative impacts on the clinker composition and therefore on the product quality observed. (An “overburning” cannot occur in the model.) By reason of potential damages on the kiln refractory and effects on the clinker composition the sintering zone temperature was adapted to the reference state by reducing the fuel input. This leads to a reduction of the specific energy demand by 2.1%. Besides the positive effects on the fuel demand the additional energy needed for the separation of air has to be taken into account. On the contrary during experiments with oxygen enrichment a positive impact on the refractory and kiln operation was reported due a higher stability of the burning conditions [Mushulovic, 2002].

Step 2: Substitution of nitrogen in cooling gas by carbon dioxide

Based on these simulation results the composition of the combustion gas was modified. The nitrogen in the cooling gas was stepwise substituted by carbon dioxide to emulate the flue gas recirculation. To avoid exhaust gases from cooler the cooling air was reduced to a level of providing secondary and tertiary air. In addition a flue gas recirculation (FGR) was calculated separately and verified by the model on a constant 21 vol.-% oxygen level. Therefore the combustion gas contained 67 vol.-% CO₂ due to the 6 % of false air. The detailed simulation results for this recirculation case are listed in Appendix 10.1. However the current results point out, that with increasing CO₂ concentration temperature profiles decrease again due to a higher specific heat capacity of CO₂ compared to N₂. From a higher heat capacity in combination with the same absorption of heat results a decrease of temperature difference. The gas is able to store more energy per mol and K. Therefore the combustion temperature is controlled by the recirculation rate. **Figure 4-20** shows the relation between of the gas temperature profile in kiln and the CO₂ concentration. It becomes evident, that by modifying the cooler, meaning reduced cooling gas, the temperature of 0 % CO₂ exceeds the reference case. Due to the different gas properties the temperature in the sintering zone decreases by complete substitution of nitrogen by carbon dioxide. Although the recirculation case does not constitute the overall optimum, it closely converges to the reference case.

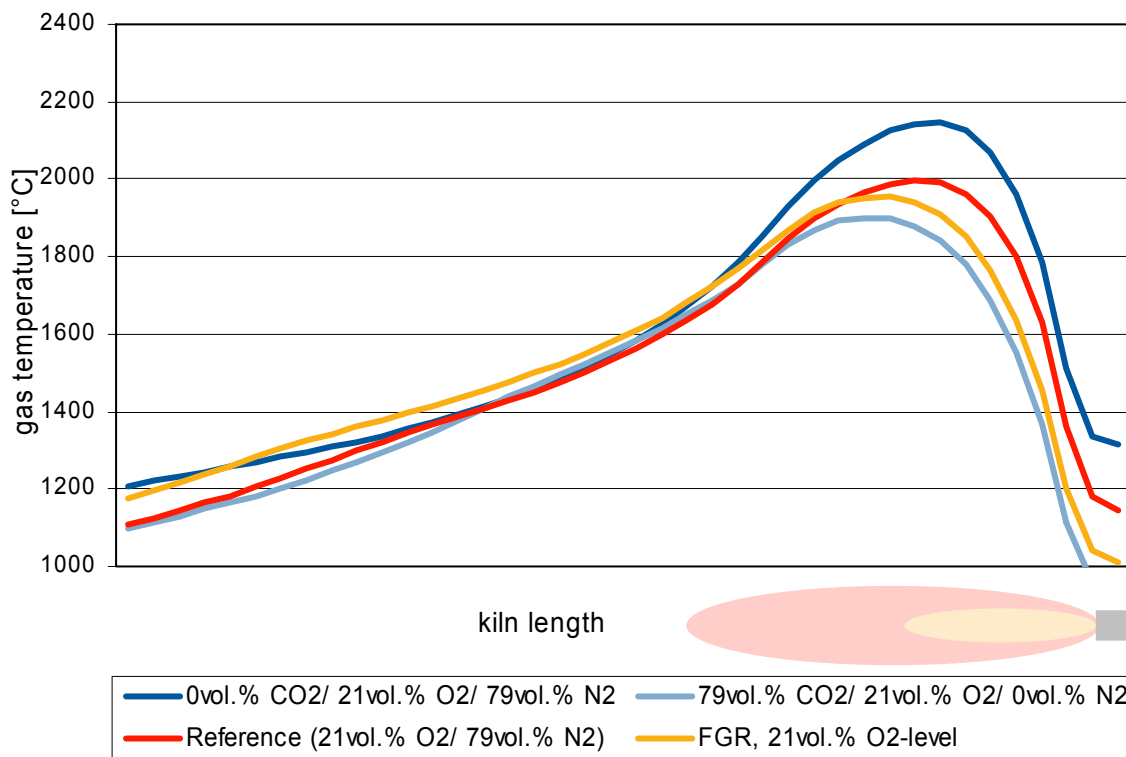


Figure 4–20 Impact of increased CO₂ concentration on gas temperature profile in kiln

Nevertheless lower gas temperatures in the kiln do not have a significant impact on the heat transfer in the kiln, because of the compensation by higher emission ratio of CO₂. In **Figure 4-21** the effect of CO₂ concentration on radiant heat is illustrated. Due to the lower tempe-

ratures in the sintering zone the radiant heat decreases as expected with increasing CO₂ concentration. However next to this zone the radiant heat increases. Compared to **Figure 4-20** the gas temperatures are similar at that point, meaning the gas containing more CO₂ possesses more energy per mol and K. Combined with the higher emission ratio the emitted energy rises. Consequently the convective heat from the wall to the material is affected in the same way. Likewise the temperature profile is affected in the preheater tower..

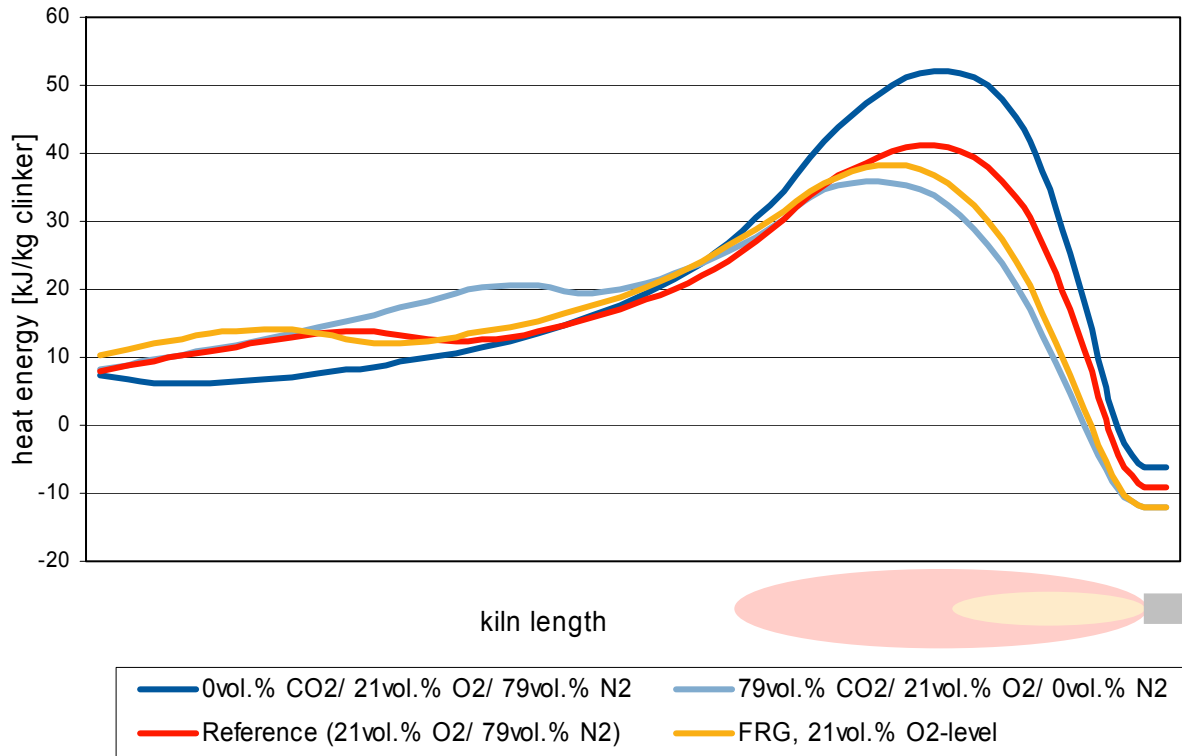


Figure 4-21 Impact of increased CO₂ concentration on radiant heat from the gas to the wall

For this reason the cold clinker composition remains unchanged by the oxyfuel operation (based upon assumptions made for the simulation calculation) although the mineralogical conversion is shifted due to the shift of heat transfer. **Figure 4-22** shows the formation shift of C₃S and C₂S clinker phases.

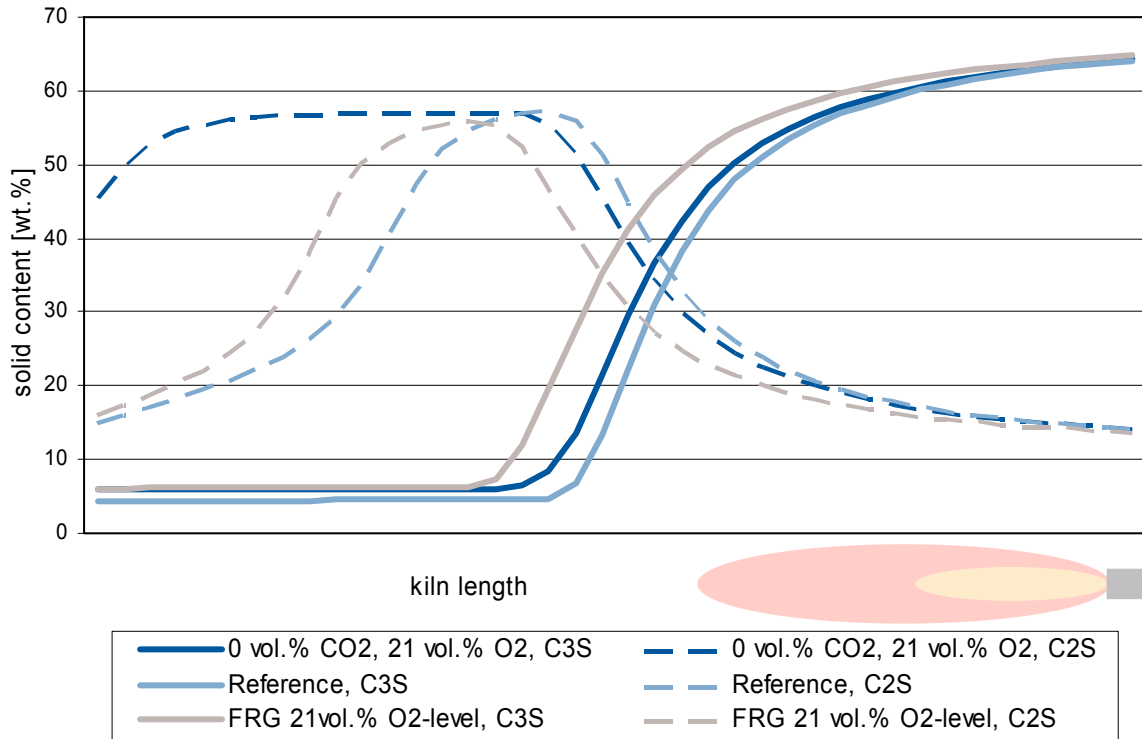


Figure 4-22 Clinker phase formation in kiln in relation to CO₂ concentration

Overall the increase of CO₂ concentration results in an energy shift in the whole kiln plant (compare **Figure 4-23**). As an indicator for this effect the cooler efficiency increases from 73 % in reference case to 86 % with maximum CO₂ concentration as a result of a reduced cooler waste air flow rate and its heat losses.

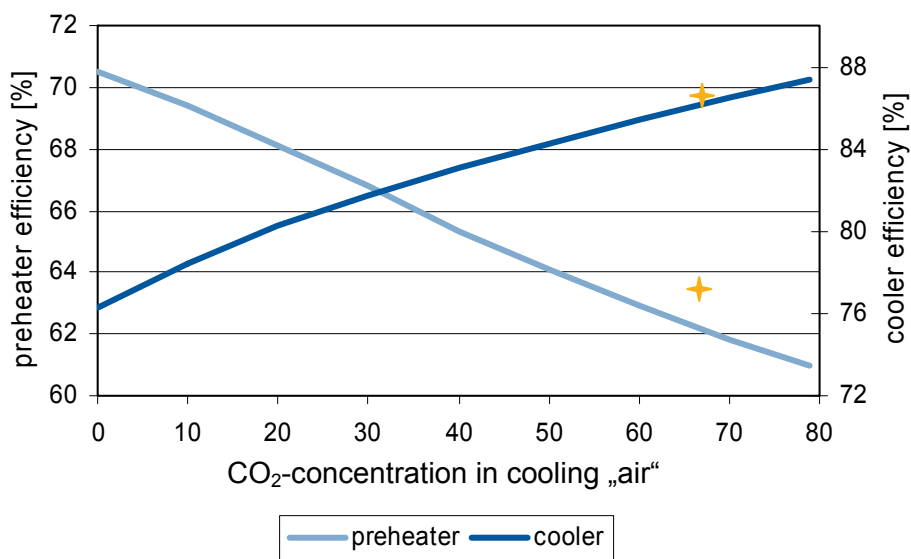


Figure 4-23 Effect of CO₂-concentration on efficiency

The cooler efficiency determines how much heat energy from hot clinker can be recuperated by secondary and tertiary air. Consequently the efficiency rises due to the increased heat capacity of carbon dioxide. Nevertheless the clinker can only be cooled down to 250°C, which makes an additional cooler stage necessary. On the contrary the preheater efficiency decreases from 68 % to 61 % due to the changing temperature profile in the preheater. The yellow crosses mark the efficiency of the FRG case at 21 vol.% oxygen level.

Finally, the maximum achievable CO₂ concentration in the raw gas is 85 vol.-% in the ideal case of complete nitrogen substitution in the cooling “air”. However, with flue gas recirculation and without reduction of air in-leaks (6 % of preheater exit gas) max. 67 vol.-% of CO₂ in the cooling gas and 78.5 vol.-% in the raw gas would be feasible for an oxygen level of 21 vol.-%. To make more detailed statements about the flue gas conditioning, which is strongly dependent on the argon content, the model scheme was enhanced by an additional gas component (argon). The kiln performance was not significantly affected by the inclusion of argon into the oxidizer composition. Moreover the nitrogen oxide content can not be calculated by the model due to the complexity of formation reactions. The resulting flue gas composition is listed in **Table 4-4**.

Table 4-4 Preheater exit gas composition for the FRG case at 21 vol.% O₂-level

Component	Vol.-%
CO ₂	78.50
O ₂	3.27
N ₂	10.30
H ₂ O	6.47
Ar	1.44
SO ₂	0.0093
Cl	0.0005

Step 3: Optimization of the oxygen content in the combustion gas

The oxygen concentration in the oxidizer becomes an additional degree of freedom, whereas the optimum level is still unknown for the clinker burning process and presumably higher than 21 vol.-%. Therefore the composition of the combustion gas was further modified based on the last simulation results. Due to the impairment of the preheater operation by a reduced gas stream, the adjustment potential of the oxygen concentration is limited. Therefore the oxygen concentration could only be increased to max. 30 vol.-%. Hence two possibilities to increase the oxygen concentration in the combustion gas have been considered. In the first scenario the oxygen mass flow to the kiln is kept constant, while the total gas flow is decreased. In the second scenario the total gas flow is kept constant, while the oxygen mass flow to the kiln was increased. The oxygen excess remains constant, consequently the clinker throughput is increased at constant specific energy consumption.

Basically the results point out, that the gas temperature in the kiln rises by 150 K by an increase to 25 vol.-% O₂ and without adapting the recirculation rate (compare **Figure 4-24**) in consequence of changing gas properties and a higher availability of oxygen. Higher temperatures in the sintering zone can be managed by optimizing the refractory brickwork. On the contrary problems with incrustation formation may occur due to the temperature increase at the kiln inlet, which makes a adjustment of fuel distribution or a shifting of the decarbonation reaction necessary. Differences between the scenarios result from the changed ratio of the specific gas volume per t of clinker. Thus it appears that the impact of CO₂ (by complete substitution of nitrogen) on the temperature profile can be adjusted by a minor increase of oxygen. Nevertheless a higher oxygen excess affects the subsequent CO₂ purification. To ensure a complete combustion the oxygen excess was fixed at a minimum of 3 vol.-% O₂ in the flue gas. That way the oxygen concentration not only poses a question of kiln operation but also of technical and economic aspects of the air separation and CO₂ liquefaction.

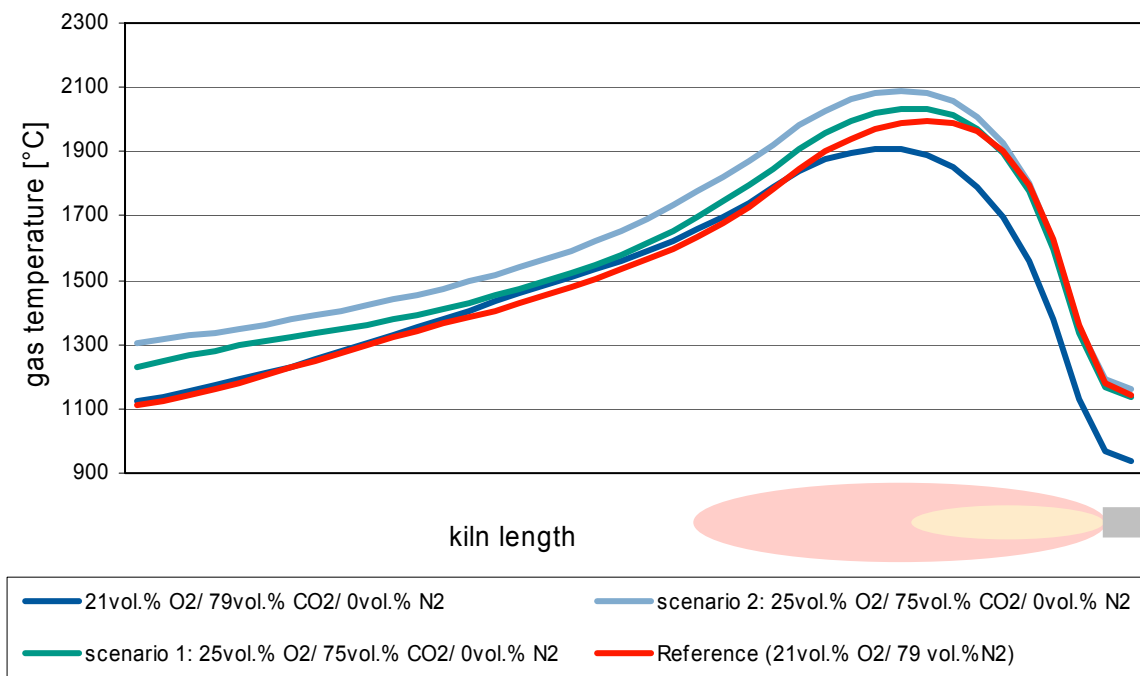


Figure 4-24 Impact of increased O₂ concentration on gas temperatures in kiln

Otherwise **Figure 4-25** shows, that even though temperatures exceed the reference case by increasing O₂ concentration, the radiant heat is nearly similar to the reference case. Generally it becomes evident, that the kiln operation can be optimized by moderate adjustment of the oxygen level. Thus the optimum oxygen level is assumed to range between 23 and 25 vol.-% using the same assumption for false air (6 % of flue gas), oxygen excess and oxidizer purity.

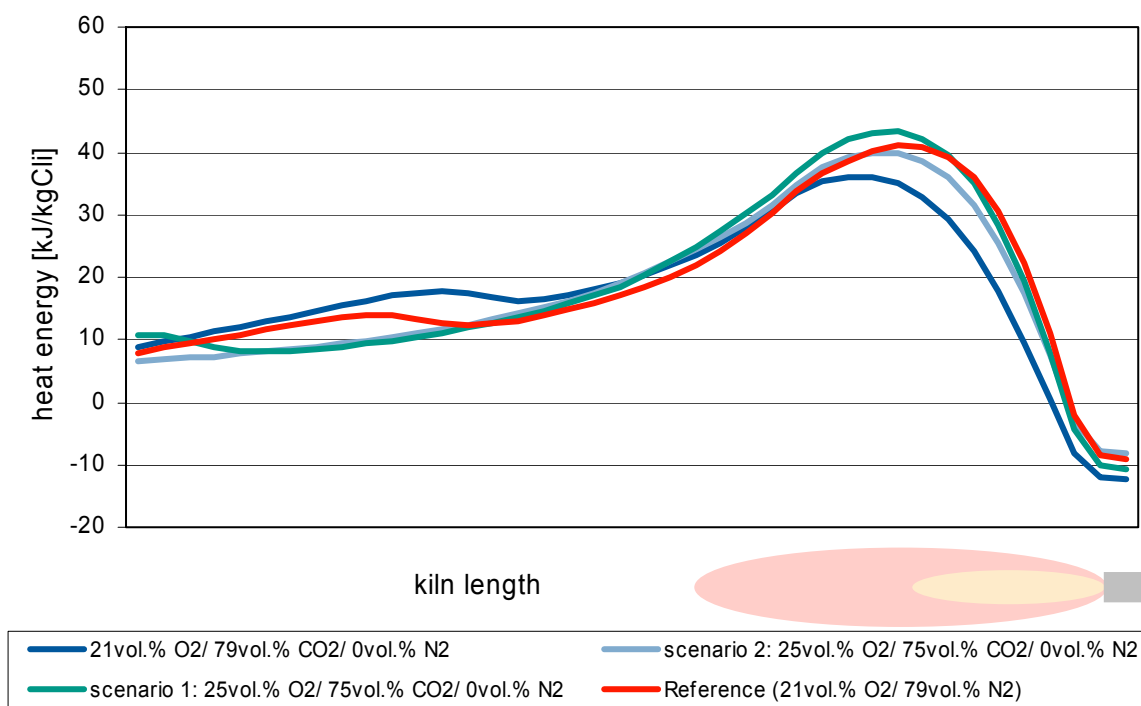


Figure 4–25 Impact of increased O₂ concentration on radiant heat in kiln

4.3.3 Cost estimation of an Oxyfuel Cement Plant

In order to allow comparison the cost estimation has been calculated based on the economic analysis for oxy-combustion CO₂ capture from IEA [IEA,2008]. The costs for CO₂ transport and storage are excluded in this estimation. Basically, a huge uncertainty of the cost estimation results from the incompletely developed technology. This calculation is based on a cement plant with a 3,000 t/d clinker capacity with a design life of 25 years, which is built in Europe. The whole plant is assumed to be built on a turnkey basis, i.e. the cost of risk is built into the contractor’s fees. Inflation was not regarded in the economic analysis. Beside the given assumptions a more detailed description of the economic analysis is published in the technical study of the IEA.

4.3.3.1 Capital Costs

Generally the configuration of the kiln plant and therefore the capital costs remained nearly unchanged relative to the base case (conventional kiln). Additional costs for the basic kiln plant are calculated solely from the modification of the cooler and the necessary sealings. A substantial increase of the costs is caused by the additional plant components around the burning process, i.e. air separation unit, CO₂ purification and compression facility, heat recovery unit. **Table 4-5** lists all included items. Variances to the IEA costs estimation arise from the differences in plant configuration. These include higher costs for the basic kiln plant due to the required two-stage cooler and larger bag filter. Moreover the air separation unit and the CO₂ purification and compression unit have to be matched to the flow rate. In the IEA

study CO₂ is only captured from the precalciner and consequently less oxygen is required. The affected plant components are smaller designed and therefore capital costs are lower. Due to the partition of the streams the IEA configuration necessitates an additional electrostatic precipitator, which is expendable in the ECRA configuration. However, a higher effort for sealing is required by the ECRA configuration since the oxyfuel operation includes the whole kiln plant.

Table 4–5 Capital costs for a new built oxyfuel cement plant

Plant component	CAPEX [Mio. €]
Cement plant	
Raw material preparation and milling	30.6
Coal preparation	10.0
Cement milling	20.0
Cement packaging and loading	13.0
Kiln plant	51.0
<i>Total costs for base plant</i>	124.6
Additional oxyfuel components	
Cryogenic air separation unit	10.9
CO ₂ purification and compression facility	9.5
Recycle stream (fans, gas mixer)	0.5
Heat recovery unit	10.0
Gas-to-gas heat exchanger	1.0
Sealings	4.0 ¹⁾
<i>Total costs for additional components</i>	35.9
Total CAPEX	160.5

1) to be discussed with suppliers

To calculate the total investment costs different items have to be added to the CAPEX. This includes design and engineering costs, costs for Engineering -Procurement -Construction (EPC) services as well as construction costs for mechanical and electrical installation, civil works, buildings and site preparation. These additional costs given in **Table 4-6** are equal to the costs given in the IEA study.

Table 4–6 Total investment costs for a new built oxyfuel cement plant

Item	Costs in Mio. €
CAPEX	160.5
Design and engineering	51.0
Construction	59.5
EPC Services	19.0
Other costs	15.0
Contingency	17.0
Fees	6.0
Owners Costs	15.0
Total Investment Cost	344

4.3.3.2 Operating Costs

Operational costs are expressed as additional costs compared to a conventional kiln and include mainly additional power costs. The calculation of the variable operating costs are based on 330 working days per year and include the costs for the raw material, fuel, process water and power demand. The quantities of the raw material components are adjusted to produce 1 Mio. tonnes of cement per year. To identify the fuel costs coal with a calorific value of 25 MJ/kg is assumed referring to an average specific energy consumption of 3,300 kJ/kg_{Clinker}. As a consequence of the temperature shift of the decarbonation reaction the energy demand increases by 90 kJ/kg_{Clinker}. This leads to an amount of 0.136 Mt/y coal (compare **Chapter 4.3.2.1**).

Table 4–7 Variable operating costs

Item	Costs in €/unit	Costs in Mio. €/y
Raw materials		5.36
Coal	65 €/t	8.02
Miscellaneous Materials		0.72
Process water	0,1 €/t	0.02
Power	0.05 €/kWh	14.36
Total variable operating costs		28.5

The starting point for the power costs calculation constitutes an overall demand of 111 kWh/t_{Cement} for a base case cement plant. In addition to this principal demand the power for O₂-supply and CO₂ purification and compression have to be accumulated. Therefore an electrical demand of 220 kWh/t_{O₂} for the ASU and 140 kWh/t_{CO₂} for CO₂ compression is

assumed. Based on a capacity of 1,000 tpd ASU and 2,500 tpd compression facility 182 kWh/t_{cement} are additionally needed. Depending on raw material moisture the flue gas enthalpy can be used for generating power by a ORC process. That way it is possible to produce 9 to maximum 12 kWh/t_{clinker} without additional firing. Summarized, the overall demand increases up to 282 kWh/t_{cement}. **Table 4-7** lists the different items, which constitutes the variable operating costs.

The IEA study provides fixed operating costs as following in **Table 4-8**. Remediation cost of the cement plant quarries are not included.

Table 4–8 Fixed operating costs for oxyfuel cement plant [IEA,2008]

Item	Costs in Mio. €/y
Maintenance	10.7
Operating labour	4.0
Supervision	0.8
Administration and general overheads	1.4
Local rates	2.9
Insurance	2.9
Total fixed operating costs	22.8

4.3.3.3 Production costs

The annual rate for the investment costs is calculated for a period of 25 years with a discount rate of 10 % and amounts to 37.9 €/t_{cement} in the case of a new installed Oxyfuel cement plant. The overall costs per tonne of produced cement were calculated from this annual rate, the fixed and the variable operating costs. **Figure 4-26** shows a comparison of the production costs in €/t_{cement} between the base case, the IEA configuration, which is applicable for retrofitting, and new built oxyfuel cement plants as described above.

It is apparent, that the most influencing factor of CO₂ capture constitutes the operating costs. Compared to the increase of 70 % of the variable operational costs, the capital costs are less affecting (increase of 27 %). Moreover it is obvious, that the costs for a new built plant exceed the retrofitting costs mainly in the operating cost due to the higher flue gas flow rate and higher oxygen demand. The fixed operating costs are assumed as equal in both cases. In their study the IEA named overall costs for CO₂ capture via oxyfuel combustion of 81.9 €/t_{cement} (increase of 24 % to base case). For new installed oxyfuel cement plants costs of 89.1 €/t_{cement} are calculated, meaning an increase of 37 % compared to current costs.

Nevertheless via retrofitting only 60 % of the produced CO₂ emissions can be captured. Therefore the additional costs per tonne of avoided CO₂ emission compared to the base case amounts to 35.8 €/t_{CO2} for retrofitting and 32.6 €/t_{CO2} in case of nearly complete capture (neglecting indirect CO₂ emissions). These costs refer to assumed emissions of 0.728 t_{CO2}/t_{cement} [IEA].

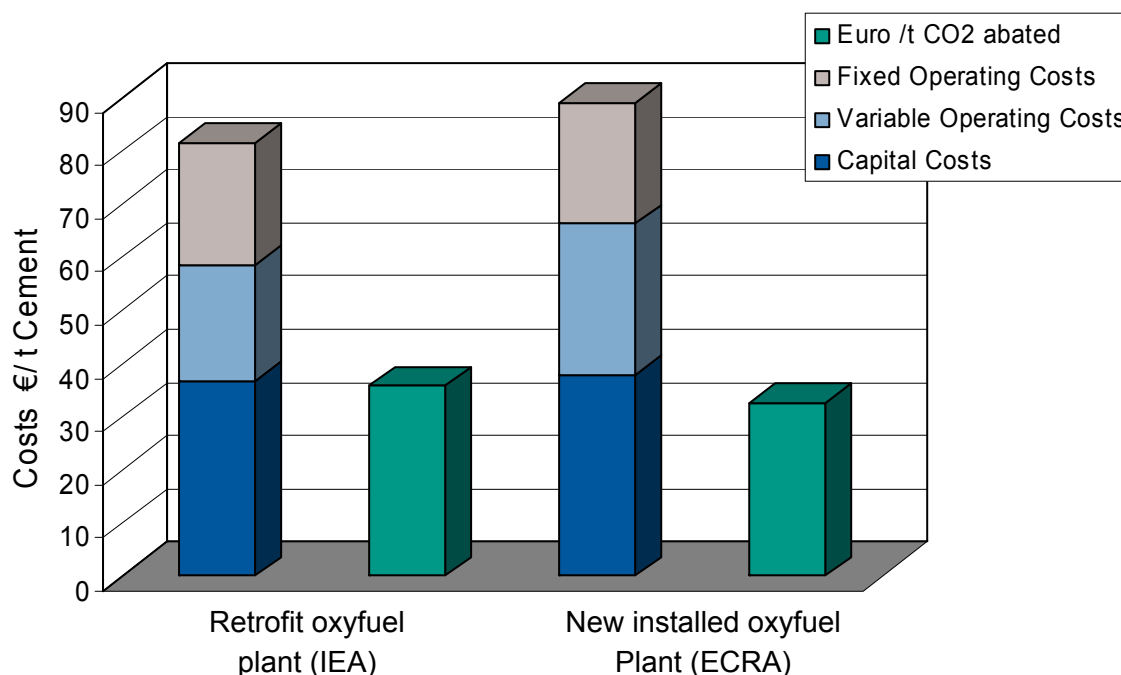


Figure 4-26 Costs in €/t_{cement} for retrofitting and a new installations

4.4 Knowledge gaps / suggestions for further work

Detailed investigations, small-scale tests

Taking all gained basic research results (temperature shift, material reactions etc.) into account an optimum operation point (recirculation rate, O₂ concentration, kiln geometry etc.) should be identified by a further comprehensive simulation study. This would allow a more detailed statement about the cost estimation beyond the one listed above. On this basis small-scale tests should follow to validate the modelling results involving besides the cement industry partners, gas supplier for chemical plant components and plant manufacture. Hence operation and safety aspects, like increasing incrustation built-up, should be elaborated for further larger-scale test.

Burner design

The burner design plays an important role in the considerations that have to be made for further steps of developing an oxyfuel cement plant. In the current modelling the primary “air” consists of nearly pure oxygen. Therefore the gas flow was reduced to keep the O₂ flow constant. It is not yet proven, whether this amount of gas suffices to form a stable flame and transport the fuel. Otherwise it has to be investigated, whether a part of the recycled gas stream should be supplied additionally to the oxidizer and how much is necessary to avoid instability of the flame. Moreover the burner design can be affected from this and might be changed.

Optimization/development

The refractory brickwork has to meet special requirements due to the changed burning conditions, like higher temperatures, influenced heat transfer and further investigation work is necessary. In Addition there is a need for further development on sealing the kiln plant. Especially the connection between static and dynamic components, i.e. at the kiln inlet and hood, poses a challenge.

4.5 Cost estimates for lab, pilot, and demo trials

Basically, the application of the oxyfuel technology for the cement industry is still in the research state. Therefore a huge uncertainty of the cost estimation results from the incomplete developed technology. By the reason of the different requirements of the power generation on the plant operation the costs estimation for demo plants are not directly transferable. (Vattenfall invested about 70 Mio. € in the construction of their pilot-oxyfuel plant "Schwarze Pumpe" including a cryogenic air separation unit and a CO₂ compression facility.) In general the operating costs are a question of overall efficiency and thus of energetic integration of the additional plant components. By this reason up-scaling becomes challenging e.g. due to the different used ASU technologies depending on the O₂ demand. The interdependencies might be others in smaller-scale like lab trials than in pilot scale.

For retrofitting a 3,000 t/d cement plant with oxyfuel technology as full scale/demo plant 90 to 100 Mio. € investment costs were mentioned [APP]. To build this plant as a complete new oxyfuel cement plant approx. 340 to 350 Mio. € have to be invested. As aspects like sealing etc. could be included in the construction considerations during design period, this might be the more reliable solution in regard to the application capability. Moreover the CO₂ reduction is limited of about 60% of the total CO₂ emissions via retrofitting a cement plant.

5 Legal issues

For the execution of CCS pilot and demonstration projects a legal and regulatory framework is required. The regulatory framework shall cover licensing procedures, site selection and qualification, liability issues, etc.

5.1 The EU Directive on geological storage of CO₂

A proposal for a Directive of the European Parliament and of the Council on the geological storage of carbon dioxide was issued in January 2008. On 17 December 2008 the Climate and Energy Package was adopted as part of a package of measures to meet the EU's target for climate protection [EU, 2009]. It is expected that the Directive will be published in the Official Journal of the European Union in April or May 2009. The Directive shall enter into force on the twentieth day following that of its publication. After that, the EU Directive has to be implemented into the national legislation of the member states within a period of two years. However, several member states are trying to implement the CCS Directive in national law as fast as possible.

As it is indicated from the title, the focus of the new Directive is the geological storage of CO₂. Capture and transport are not addressed in the Directive. The issue of CO₂ capture is regulated under the so-called IPPC Directive (96/61/EC).

The most important contents of the EU Directive can be summarized as follows:

- The geological storage of CO₂ – onshore and offshore – is regulated.
- Storage in the water columns is prohibited (due to great environmental risks).
- CO₂ captured and stored is recognised as not emitted under the ETS
- Storage outside the European Union is not banned, but CO₂ which is stored so will receive no credit under the European ETS.
- Demonstration or research projects are not covered by the Directive.
- When EHR (Enhanced Hydrocarbon Recovery) is combined with geological storage of CO₂, the provisions of the Directive will apply.
- No information about the minimum CO₂ purity is given, because the achievable CO₂ concentration depends on the applied capture technology. Furthermore the characteristics of the storage site are important for the tolerable impurities. As a result of this, no limit values were stipulated in the Directive. The Directive says, that "a CO₂ stream shall consist overwhelmingly of carbon dioxide".
- The Directive provides a "**capture ready**" provision for large combustion plants. All new built combustion plants with an electrical out put > 300 MW shall have suitable space on the site for CCS equipment to be retrofitted.
- In the framework of the licensing procedures, also other EU Directives are covered, e.g. the IPPC Directive and the EIA Directive (Environmental Impact Assessment).

- The storage site shall be transferred to the competent authority on its own initiative or upon request from the operator, if and when all available evidence indicates that the stored CO₂ will be completely contained for the indefinite future.
- The operator is liable for any damage caused during the operation in the post-injection phase (until the responsibility is transferred to the member state). The insurance industry will offer liability coverage.
- According to the "polluter pays" principle the operator keeps the responsibility for the storage site. After a minimum period of 20 years, the can be transferred to the Member State control.
- Third party access to the transport and storage network is guaranteed.

With the European CCS Directive, a first step to an legal framework towards geological sequestration of CO₂ was made. Based on that, the planning of CCS demo projects can be continued.

At the moment the European Commission is considering to include CO₂ as named substance in the revised Council Directive 96/82/EC on the control of major-accident hazards involving dangerous substances (Seveso Directive) with suitable threshold values [EU, 1997]. In this case the Commission would also propose to change Annex III of the Environmental Liability Directive [EU, 2004].

5.2 National regulations

As already mentioned, the EU Directive on geological storage of CO₂ will be published in April or May 2009. After that, the member states have to implement the Directive into their national law within two years. However, UK has already implemented national regulations for CO₂ storage, which enter in force in April 2009. In Germany, the implementation process is being carried out at the moment so that a national law could be given in summer 2009.

In the US, the interdisciplinary project CCSReg is being carried out, which shall develop recommendations for how best to regulate the processes of CO₂ capture, transport and storage in deep geological formations [CCSReg, 2008]. A draft version of a so-called "American Clean Energy and Security Act of 2009" was issued recently, containing regulations about clean energy (incl. CCS), energy efficiency, global warming etc. [USA, 2009]. CCS is seen as a method to reduce global warming pollution by capture and storage of carbon dioxide. The draft includes a CCS early demonstration programme, incentives for the wide-scale commercial deployment of CCS, and performance standards for new coal-fired power plants.

The Australian "Regulatory guiding principles for CO₂ capture and geological storage" is one of the first legal frameworks for CCS.

5.3 Public acceptance

Apart from all legal issues, a CCS project can only be carried out successfully, if the technology has gained acceptance from the general public. Therefore, pioneering public consulta-

tion work has to be done at local level. The public awareness should be focused on projects and local issues rather than on the general concept of CCS. It is very important that the population in the vicinity of a storage site is informed from the very beginning about a planned storage project and that they feel safe. For this purpose, the operator of a storage site should organize local meetings and should issue information in the local newspapers etc.

6 Transport and Storage

Transport and storage of CO₂ are essential components of the CCS chain but this issue is not cement-specific and thus not subject of the ECRA CCS project. Nevertheless a study about CO₂ storage was carried out in the framework of the ECRA project, including also some aspects of CO₂ transport [Abbate, 2008]. Therefore the following chapter gives only a short impression about the challenges to establish a transport and storage infrastructure.

6.1 CO₂ transport

The transport of the separated CO₂ from the emission source to the storage site can be carried out by pipelines, ships, trains and trucks. However, a simple example shows that for larger amounts of CO₂ only pipeline transport is a viable option. The transport of 5 Mio. tonnes of CO₂ could be carried out by:

- 1 pipeline (0.5 m diameter)
- 300 ships
- 5,000 train transports
- 250,000 truck transports

Ship transport can only be economical if CO₂ has to be moved large distances over water. Road and rail transports could only be used on a limited basis for small-scale shipments of CO₂, e.g. from research projects.

According to IEA estimates, 6 Gt CO₂ per year could be captured in 2050 - an equivalent of about 6,000 Sleipner projects (see chapter 6.2; one of the first commercial storage projects). This number shows which extraordinary efforts will be necessary to erect a sufficient pipeline infrastructure in the years to come, meaning unique challenges in financing, site selection, access rules, etc. Up to now, there is almost no CO₂ pipeline infrastructure available in Europe. In the USA, a CO₂ pipeline system of more than 3,000 miles is existent.

For the conduction of the announced CCS pilot projects, the major energy companies are planning pipelines for CO₂ transport. For example, the German energy company RWE intends to build a 400 km pipeline from western Germany (IGCC demo project in Hürth) to the north of Germany, where potential storage sites are investigated at the moment. In an early state of CCS with only a few demonstration projects, a point-to-point transport from the emission source to the storage site is likely. At a later stage, when CCS is in a commercial state, regional clusters are expected which could be connected to the pipeline network.

The costs of pipelines can be classified in the following categories:

- Construction costs:
 - material/equipment costs (pipe, pipe coating, cathodic protection, telecommunication equipment; possible booster stations)
 - installation costs (labour)

- Operations and maintenance costs:
 - monitoring costs
 - maintenance costs
 - energy costs

- Other costs:
 - design
 - project management
 - regulatory filing fees
 - insurance costs
 - right-of-way costs, etc.

The investment costs are higher when compressor station(s) are required to compensate pressure losses along the route. A characteristic range for the compression pressure could be >70 to >100 bar. In general, the required pressure depends on the transport distance. Furthermore the diameter of the pipeline influences the investment costs, ranging from 0.1-0.2 Mio. US\$/km for a diameter of 0.1 m up to 0.75-1.5 Mio. US\$/km for a diameter of 1.2 m.

The investment costs also depend on the terrain. The costs may increase by 50 to 100% or more when the pipeline route is congested or highly populated and urbanized. Costs change as well in mountains, in nature reserve areas, in areas with obstacles such as rivers and freeways. Furthermore, steel prices have a significant impact on the investment cost for a transport infrastructure.

Besides the economic aspects, the operational reliability and safety of CO₂ pipelines is an important issue. There is a need to develop and apply appropriate standards for pipeline design, construction and operation. Furthermore it is essential to control the risks of CO₂ pipeline transport. Therefore scenarios about potential accidents have to be assessed and the conclusions have to be drawn.

6.2 CO₂ storage

The long-term storage of CO₂ is currently subject to public discussions. Whereas CO₂ capture is seen only as a technology for a transmission period, a safe storage of CO₂ - without the risk of any leaks - has to be guaranteed for hundreds and thousands of years. Many research projects are carried out all over the world to identify and qualify potential CO₂ storage sites. However, up to now only a few large-scale (commercial) CO₂ storage projects are operating worldwide:

- the Sleipner project in Norway (1 Mio. t/y)
- the Weyburn project (with EOR) in Canada (1.8 Mio. t/y)
- the In Salah project in Algeria (1 Mio. t/y).

The current European CO₂-SINK project is dealing with research on geological storage of CO₂. Under the management of the German Research Centre for Geosciences (GFZ) in cooperation with 18 partners from nine countries, the injection into and storage of CO₂ in deep, saltwater-filled, porous rocks is examined for the first time Europe-wide. In 2008, GFZ started with the underground storage of CO₂ in Ketzin. Up to 60,000 tonnes of CO₂ will be stored at a depth of more than 600 m within 2 years. Until 12 April 2009, 12.663 tons of CO₂ were injected in the underground.

Within the framework of other European research projects, overviews about potential storage sites were established. The European GESTCO project gave a database for potential storage sites in Western Europe. The current European project GEOCAPACITY will extend the database to countries in Middle and Eastern Europe.

The major energy companies, which are planning CCS pilot or demo projects, are exploring also potential storage sites. For example, the Vattenfall company is investigating the possibility of storing CO₂ at the Vedsted Structure in Northern Denmark, which is a geological reservoir at a depth of between one and two kilometres below the surface. Therefore, 2D and 3D seismic surveys are carried out and at a later stage appraisal drillings. The aim of these investigations is to confirm the expectations regarding storage capacity, injectivity and structural containment, indicating that the geology of northern Jutland would be well suited for the safe, long-term storage of CO₂. Based on the results obtained, an investment decision about a full-scale post-combustion demonstration plant will be made. The captured CO₂ would be transported through a 30 km pipeline to the storage site.

An important precondition for the conduction of the planned storage project was the adoption of the European Directive on the geological storage of CO₂, which is a first legal framework for storage projects in Europe. At the latest in 2011, all the member states of the European Union should have also a national legislation about CO₂ storage.

In summary it can be said, that the exploration of potential storage sites is under way – both for research and also for commercial projects. It can be expected that the national authorities will establish registers about storage sites in the next years. As a third-party access to the transport and storage infrastructure is guaranteed, there is no need for cement companies to operate a storage site.

7 The way to a commercial stage of CCS – incentives and funding

The European Union has affirmed its statement that climate protection is a prior issue on the political agenda. The objective of the EU is to make CCS commercially viable by 2020. Therefore a series of demonstration projects has to be carried out. Financing and incentivisation of the demonstration projects shall be enabled through funding by the European Union. Besides that, support from the national governments would be vital to initiate CCS demonstration projects. It is obvious that the power industry is the leading industrial sector for the conduction of the first pilot and large-scale demo projects. However, also a contribution from other industries is required to achieve the target values for CO₂ reduction.

To achieve this goal, the European Union has approved 1.05 billion € of funding for CCS projects in March 2009. The money comes from a 5 billion € budget surplus. Under the plan, Germany, the UK, Poland, the Netherlands and Spain will all receive 180 Mio. € each, Italy will receive 100 Mio. € and France will receive 50 Mio. €. The French project will capture and store CO₂ from a steel plant. Furthermore, ETS will be a source of CCS support, namely the revenues from 300 Mio. CO₂ allowances shall be awarded for further demo projects in other industrial sectors.

It is generally accepted, that during the demonstration phase incentives would be necessary to encourage a CCS project, meaning that a funding is absolutely necessary to fill the economic gap. In the long-term, a higher carbon price and reduced cost of CCS should be enough of an incentive. It can be expected that CCS costs will come down over time. In a commercial phase of CCS, the costs should reach similar levels as CO₂ allowance prices or be even lower.

The Commission has emphasised, that not only various capture technologies shall be investigated, but also various emissions sources shall be included in the CCS demo projects. Besides, it is important to demonstrate industrial CCS not only at new plants, but also retrofits. The cement industry as a sector with significant CO₂ emissions would be a good candidate to be included in the demo programme and should therefore consider to apply for such a project.

It is expected, that the results from post-combustion pilot and demo trials in power plants can be transferred – in a limited degree – to the clinker burning process. Therefore there will be a significant gain of knowledge or scientific insight in the next years, so that at least a pilot trial in the cement industry could be planned with limited risks.

International cooperation and exchange of ideas will be essential on the way to a commercial state of CCS. For these purposes, the so-called "Global Carbon Capture and Storage Institute" (GCCSI) was launched on 16 April 2009 in Canberra, Australia. The Institute, which was established by the Australian Government, shall accelerate the deployment of CCS technologies globally and facilitate the sharing of information. Up to now, 85 bodies have signed as members and collaborating participants [Australia, 2009]. The Australian Government will provide an annual funding of 100 Mio. \$.

8 Summary

In 2007, the European Cement Research Academy ECRA has started a research project on the potential application of carbon capture technologies in the cement industry. The project is divided into at least four phases. Phase I of the project was completed in summer 2007 and resulted in an overview about all the carbon capture technologies, including an assessment about the applicability at the clinker burning process. According to that, chemical absorption technologies and oxyfuel combustion were the most promising measures for a future application at cement kilns. Therefore the next step of the research project should focus on those technologies.

Accordingly the present report provides more information about the potential application of post-combustion (chemical absorption) and oxyfuel technologies at the clinker burning process. Thereby a basis for the decisions about the next steps of the ECRA research project shall be given, which would include at least small-scale trials to close the current knowledge gaps.

The investigations about chemical absorption processes focused on the following issues:

- A survey about the flue gas characteristics which is important for the general process design and the required abatement of other exhaust gas components like SO_2 and NO_x . The SO_2 concentration should be less than 80 mg/m^3 , because it reacts irreversible with the amine solvent; for certain solvents like MEA or MDEA, SO_2 should be low as possible ($< 30 \text{ mg/m}^3$). The NO_2 concentration should not exceed 40 mg/m^3 (NO does not react with amine absorbents like MEA etc.), which should be achievable with the application of SNCR.
- A plant layout was designed for the implementation of a chemical absorption process at the clinker burning process.
- Investigations regarding solvent regeneration showed that an auxiliary power block would be necessary to provide the energy for the regeneration of the absorbent (i.e. low-pressurized steam).
- A compilation of cost figures was given which were mainly determined within two external studies. According to that, the calculated investment costs showed a great range – resulting from about 100 Mio. € to almost 300 Mio. €.

The investigations about chemical absorption technologies resulted in the conclusion that next step of an ECRA research project should include a detailed modelling of the capture process, an improved integration concept based on the results of the modelling process and also laboratory trials about the degradation behaviour of the relevant solvents. It is expected that external funding would be necessary to finance the required research activities.

In the Phase I report, membranes were seen as a promising alternative post-combustion technology for CO_2 capture – though they were developed only on a research level. During the last two years no significant step forward was achieved with membrane technologies. Up to now no results from small-scale or pilot project are known where membranes are used to separate CO_2 from a flue gas stream. Nearly all the post-combustion pilot projects, which were announced by the power sector, are focussing on chemical absorption technologies. Therefore, the ECRA report does not include more detailed assessments about membranes, but the membrane issue will stay on the agenda of the ECRA project in the years to come.

In contrast to post-combustion CO₂ capture, oxyfuel combustion would influence significantly the clinker burning process. Therefore, more basic investigations about the clinker burning process had to be carried out. Within the framework of the ECRA project, a possible configuration of an oxyfuel cement plant was designed, using an established process model. The oxygen demand was calculated and furthermore the required oxygen purity. Moreover, the subsequent steps of CO₂ purification and compression were included in the overall assessment of the oxyfuel process. Furthermore the interdependency between these chemical plant components was pointed out. For the energetic dimensioning aspects like the raw material drying and heat recovery posed problems. Simulations via the process model showed an energy shifting in the kiln plant as a consequence of higher CO₂ concentration in the kiln atmosphere due to the different gas properties compared to N₂. By adjusting the oxygen concentration it is possible to compensate this affect of the CO₂. As a result of insufficient sealings the wet flue gas would contain under 80 vol.-% CO₂ from today's perspective.

Apart from the modelling process, also laboratory trials were conducted to find out the impact of the oxyfuel combustion on the burning process. In particular, the influence of an increasing CO₂ partial pressure on the relevant chemical and mineralogical reactions was investigated. The investigations showed an increase of the reaction enthalpy due to a temperature shift of the decarbonation reaction. As a result of it, a higher temperature in the calciner would be required which could cause problems with the refractories and with burning low calorific secondary fuels.

Costs for avoided CO₂ emissions via oxyfuel combustion were calculated to 32.6 €/t_{CO₂} at overall costs for CO₂ capture of 89.1 €/t_{cement}. The main factor on the costs states the operating costs due to the energy intensive air separation and CO₂ compression.

In the next steps an optimum operation point should be identified by a further comprehensive simulation study. On this basis small-scale tests should follow to validate the modelling results and elaborate operation and safety aspects for lager-scale tests. Beyond this further development and optimization should be done in the sector of burner design, sealing and refractory.

Transport and storage of CO₂ are essential steps in the full CCS chain. If the cement industry would start a pilot or demo project, a transport and storage infrastructure should be available. However, it is not likely that cement companies would operate a pipeline network or a storage site. Therefore the ECRA project is not focussing on those steps of CCS. Nevertheless the international activities on the transport and storage sector shall be observed and reflected in the ECRA reports.

Subject to the provisions of the Technical Advisory Board a research agenda is proposed for Phase III of the research project. Though a lot of information about chemical absorption technologies is available, there are knowledge gaps regarding a potential application at cement kilns.

To reach the CO₂ reduction targets, research activities, pilot and demo projects are required in the relevant industries, not only on a national level, but also all over Europe and world-wide. There is a need to demonstrate the applicability of CCS globally, in order to assess the potential of this technology, climb the learning curve and drive down costs. This means a significant increase in resources, both financial and also human. It can be assumed that

there will a sufficient public funding to conduct the required research work. Therefore it should be considered to participate in the international CCS research programmes, which would mean at least a pilot trial at a cement kiln. It can be assumed that chemical absorption technologies will be developed to a pre-commercial state so that a small-scale trial at a cement kiln could be performed without major risks. A sufficient public funding would be required to close the existing economic gap.

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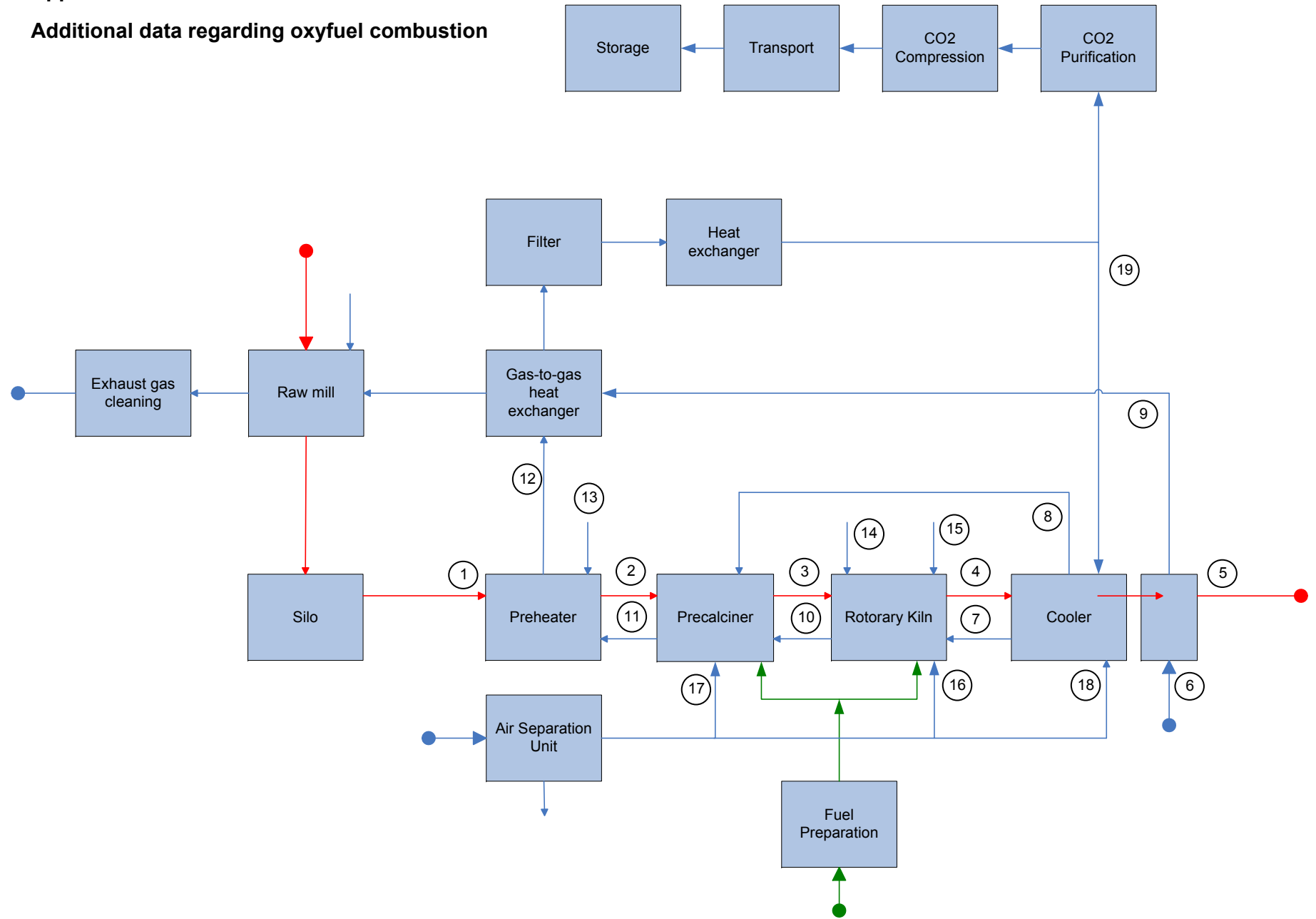
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10 Appendix

10.1 Additional data regarding oxyfuel combustion



Number	1	2	3	4	5
Condition	Solid	Solid	Solid	Solid	Solid
Description	raw meal	preheated material	kiln feed	hot clinker	cold clinker
Mass flow [kg/h]	200025	232544	147915	131510	124989
Temperature [°C]	60	781	868	1423	278
Components [wt.%]					
Al ₂ O ₃	3,257	2,558	0,035	0,004	0,004
CaCl ₂	0,000	0,000	0,000	0,000	0,000
CaCO ₃	77,339	62,246	4,677	0,000	0,000
CaO	0,000	9,278	41,844	0,579	0,579
CaSO ₄	0,000	0,012	0,055	0,000	0,000
Cl	0,000	0,000	0,000	0,000	0,000
Cl-	0,000	0,000	0,001	0,015	0,015
C _{org}	0,100	0,000	0,000	0,000	0,000
Fe ₂ O ₃	1,964	1,541	0,012	0,001	0,001
H ₂ O	1,002	0,000	0,000	0,000	0,000
K	0,291	0,152	0,000	0,000	0,000
K ₂ SO ₄	0,352	0,700	1,139	1,127	1,127
KCl	0,016	0,253	1,058	0,000	0,000
KCl I	0,000	0,038	0,182	0,199	0,199
MgCO ₃	1,494	1,203	0,090	0,000	0,000
MgO	0,000	0,181	0,818	0,011	0,011
Mn ₂ O ₃	0,050	0,039	0,000	0,000	0,000
Na	0,057	0,030	0,000	0,000	0,000
Na ₂ SO ₄	0,095	0,188	0,300	0,307	0,307
NaCl	0,004	0,066	0,275	0,000	0,000
NaClI	0,000	0,007	0,035	0,039	0,039
P ₂ O ₅	0,040	0,048	0,078	0,081	0,081
SiO ₂	13,829	14,122	14,184	0,030	0,030
Sulfide	0,050	0,001	0,000	0,000	0,000
TiO ₂	0,060	0,047	0,001	0,000	0,000
C3S	0,000	1,190	6,025	64,875	64,875
C2S	0,000	3,027	15,185	13,583	13,583
C3A	0,000	0,230	1,163	10,099	10,099
C4AF	0,000	0,191	0,966	8,407	8,407
CA	0,000	1,622	7,277	0,000	0,000
C2F	0,000	1,031	4,598	0,642	0,642
degree of decarbonation	0,0	27,7	95,9	100,0	100,0

Number	6	7	8	9	10	11	12
Condition	Gas	Gas	Gas	Gas	Gas	Gas	Gas
Description	cooling gas	secondary air	tertiary air	cooler exhaust gas	kiln gas out	calciner gas out	raw gas
Volume flow [m ³ /h]	108369	135461	322053	325758	189268	604617	365122
Volume flow [m ³ /h] (stp)	102727	29091	73535	130303	36410	144814	153802
Volume flow [m ³ /h] (stp, dry)	101700	28800	72800	129000	33681	137406	143844
Temperature [°C]	15	999	923	280	1147	867	375
Pressure	1013,25	1013,25	1013,25	1013,25	1013,25	1013,25	1013,25
Components [vol.-%]							
Ar	2,000	2,000	2,000	0,900	1,838	1,499	1,444
CaCl ₂	0,000	0,000	0,000	0,000	0,000	0,000	0,000
CaSO ₄	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Cl	0,000	0,000	0,000	0,000	0,002	0,001	0,000
CO	0,000	0,000	0,000	0,000	0,000	0,000	0,000
CO ₂	67,000	67,000	67,000	0,000	76,519	82,369	78,496
H ₂	0,000	0,000	0,000	0,000	0,000	0,000	0,000
H ₂ O	1,000	1,000	1,000	1,000	7,495	5,116	6,474
O ₂	21,000	21,000	21,000	21,000	2,085	3,015	3,274
K	0,000	0,000	0,000	0,000	0,000	0,000	0,000
K ₂ SO ₄	0,000	0,000	0,000	0,000	0,033	0,000	0,000
KCl	0,000	0,000	0,000	0,000	1,235	0,000	0,000
N ₂	9,000	9,000	9,000	77,100	10,270	7,984	10,302
Na	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Na ₂ SO ₄	0,000	0,000	0,000	0,000	0,003	0,000	0,000
NaCl	0,000	0,000	0,000	0,000	0,410	0,000	0,000
SO ₂	0,000	0,000	0,000	0,000	0,109	0,017	0,009
dust content [g/m ³] (stp)	0,00	64,12	64,12	64,12	342,29	334,89	65,30

Number	13	14	15	16	17	18	19
Condition	Gas	Gas	Gas	Gas	Gas	Gas	Gas
Description	false air preheater+calciner	false air kiln inlet	false air kiln hood	primary air, kiln	primary air, calciner	Oxidizer	Recirculated raw gas
Volume flow [m ³ /h]	7071	1111	303	2117	474	19482	83049
Volume flow [m ³ /h] (stp)	7071	1111	303	2117	474	18482	83049
Volume flow [m ³ /h] (stp, dry)	7000	1100	300	2117	474	19482	82218
Temperature [°C]	15	15	15	15	15	15	15
Pressure	1013,25	1013,25	1013,25	1013,25	1013,25	1013,25	1013,25
Components [vol.-%]							
Ar	0,900	0,900	0,900	3,500	3,500	3,500	1,520
CaCl ₂	0,000	0,000	0,000	0,000	0,000	0,000	0,000
CaSO ₄	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Cl	0,000	0,000	0,000	0,000	0,000	0,000	0,000
CO	0,000	0,000	0,000	0,000	0,000	0,000	0,000
CO ₂	0,000	0,000	0,000	0,000	0,000	0,000	83,000
H ₂	0,000	0,000	0,000	0,000	0,000	0,000	0,000
H ₂ O	1,000	1,000	1,000	0,000	0,000	0,000	1,000
O ₂	21,000	21,000	21,000	95,000	95,000	95,000	3,500
K	0,000	0,000	0,000	0,000	0,000	0,000	0,000
K ₂ SO ₄	0,000	0,000	0,000	0,000	0,000	0,000	0,000
KCl	0,000	0,000	0,000	0,000	0,000	0,000	0,000
N ₂	77,100	77,100	77,100	1,500	1,500	1,500	10,900
Na	0,000	0,000	0,000	0,000	0,000	0,000	0,000
Na ₂ SO ₄	0,000	0,000	0,000	0,000	0,000	0,000	0,000
NaCl	0,000	0,000	0,000	0,000	0,000	0,000	0,000
SO ₂	0,000	0,000	0,000	0,000	0,000	0,000	0,000
dust content [g/m ³] (stp)	0,00	0,00	0,00	0,000	0,000	0,000	0,000