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Process Simulation of Oxy-combustion CO₂ Capture in Cement Plant

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MASTER THESIS

for

Student Maria Magnussen Skinnemoen

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Process simulation of oxy-combustion CO₂ capture in cement plant
*Prosess-simulering av oksy-forbrenning CO₂ fangst i sementanlegg***Background and objective**

The cement industry contributes to approximately 5% of the global man-made CO₂ emissions. In addition, a large cement plant is a big point source of CO₂ emissions and the flue gases has a relatively high CO₂ content. CO₂ capture from a cement plant is therefore interesting as part of a mitigation plan for decreasing the global CO₂ emissions.

The main portion of the CO₂ emissions in a cement plant originates from the calcination of CaCO₃ (limestone) into CaO and CO₂ according to:



The CaO is further used for the production of cement. Not only is CO₂ a product in the calcination reaction, but the reaction is endothermic and heat has to be supplied. Normally, this heat is partly supplied by combustion of a fossil fuel leading to further CO₂ formation and emission.

Possibilities for CO₂ capture range from post-combustion methods to oxy-combustion capture, including combination thereof. The thesis work will focus on oxy-combustion CO₂ capture. The work would be related to the NORDICCS project where the potential for CCS in the Nordic region is investigated. Of special interest would be the Norcem cement plant in Brevik, Norway.

The objectives of the thesis work are to model and simulate oxy-combustion CO₂ capture in a cement plant. A process simulation tool like Aspen HYSYS should be used. As a starting point, student Jelmer de Winter's project work should be utilized. In addition to the process simulations, an engineering evaluation of the necessary modifications to the cement process should be conducted.

The following tasks are to be considered:

1. Review of literature related to oxy-combustion CO₂ capture and cement production.
2. Process simulation of the calcination process with varying degree of air leakage where the heat is supplied by combustion in oxygen followed by capture of the CO₂.
3. Evaluate further gas separation after H₂O condensation to achieve needed CO₂ quality.
4. Evaluation of necessary cement process modifications and analyze operational risks due to the modifications.

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- Field work

Department of Energy and Process Engineering, 14. January 2014



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Preface

This master thesis ends my 5-year Master of Science degree in Energy and Environmental Engineering at the Norwegian University of Science and Technology (NTNU) in Trondheim, Norway. The thesis was written at the Department of Energy and Process Engineering, and is an extension of the project thesis “Process Simulation of CO₂ Capture in a Cement Plant”, written by Stud.Tech. Jelmer de Winter in the fall 2013.

The formal supervisor for the thesis has been Professor Olav Bolland, and the person responsible for the follow up has been Associate Professor Lars O. Nord. I would like to thank the Department for the support and in particular my supervisor Lars O. Nord for his time and guidance throughout the semester. I would also like to thank Post.doc. Chao Fu for his assistance regarding the air separation unit and the CO₂ compression and purification unit.

Trondheim, 25th June, 2014



Maria Magnussen Skinnemoen

Abstract

The objectives of this master thesis have been to model and simulate oxy-combustion CO₂ capture in a cement plant. The model developed is a process simulation of the calcination process with varying degree of air in-leakage, where heat is supplied by combustion in an oxygen rich environment, followed by capture of the CO₂. The further gas separation after H₂O condensation to achieve the required CO₂ quality was evaluated. In addition to the process simulations, a review of literature related to oxy-combustion CO₂ capture and cement production was performed, and an engineering evaluation of the necessary modifications to the cement plant conducted.

A simulation model was built in Aspen HYSYS, and student Jelmer de Winter's project work was utilized as a starting point. The model was developed with the aim to achieve results comparable to a process model constructed by the European Cement Research Academy (ECRA) in 2009. The goal was to capture as much of the CO₂ as possible, and to achieve a CO₂ purity of minimum 95 mol-% after the CO₂ Compression and Purification Unit (CPU).

CO₂ purity in the dry flue gas of ~85 mol % was achieved, with a CO₂ capture rate up to 96.4 %. Five different air in-leakages (2, 4, 6, 8 and 10 % of total flue gas flow) were tested. The results showed that the CO₂ concentration in the flue gas decreased with increasing degree of air in-leakage. The decrease in CO₂ concentration causes an increase of the power consumption of the CO₂ CPU of ~2.6 % per percentage point of air in-leakage, and the CO₂ capture rate was also reduced when the air in-leakage increased. These results agree well with results from previous oxy-combustion studies, and show the importance of minimizing air in-leakages in the cement plant.

If oxy-combustion capture is to be utilized at a cement plant, some process modifications and additional equipment is required. An Air Separation Unit (ASU) is needed to provide almost pure oxygen for the combustion process. A Compression and Purification Unit (CPU) is also required, in order achieve the necessary CO₂ purity and transport conditions.

When using oxy-combustion technology, both the material conversion in the cement kiln system and the operational specifications of the overall process are different from those in conventional kiln operation. However, research made by ECRA in 2012 showed that the negative impacts of oxy-combustion on the product quality seem to be negligible.

Other necessary process modifications when retrofitting with oxy-combustion are news design of the kiln burner and the clinker cooler in the cement plant. In addition, prevention of excessive air in-leakage by improving sealing locations at the cement plant is necessary, as the simulation results show. This is possible e.g. by waste gas flushed systems, or by an improved maintenance of inspection doors and similar devices. The CPU is up to a certain point capable of handling changes in the flue gas composition at short-term inspections; however it limits its efficiency.

Sammendrag

Formålet med denne masteroppgaven har vært å modellere og simulere CO₂-fangst ved hjelp av oksy-forbrenning i et sementanlegg. Modellen som er utviklet er en prosesssimulering av kalsinerings-prosessen med varierende grad av falsk luft (luftinntrengning), hvor tilført varme stammer fra forbrenning i et oksygenrikt miljø, etterfugt av fangst av CO₂. Gasseparasjonen etter H₂O-kodensasjon i prosessen for å oppnå ønsket CO₂-kvalitet er evaluert. I tillegg til prosesssimuleringene, ble et litteraturstudium om oksy-forbrenning CO₂-fangst og sementproduksjon utført. Nødvendige prosessmodifikasjoner av sementanlegget og operasjonsrisikoer ved disse er vurdert.

En simuleringsmodell er utviklet i Aspen HYSYS. Student Jelmer de Winters prosjektoppgave fra 2013 har blitt brukt som utgangspunkt for denne modellen. Modellen ble utviklet for å oppnå sammenlignbare resultater som en prosessmodell laget av European Cement Research Academy (ECRA) i 2009. Målet har vært å fange så mye CO₂ som mulig, og å oppnå en en CO₂-renhet på minimum 95 mol-% etter CO₂-reanseanlegget.

CO₂-renheten i den tørre røykgassen på 85 mol-% ble oppnådd, med et CO₂-fangst-forhold opp mot 96.4 %. Fem ulike grader av falsk luft (2, 4, 6, 8 og 10 % av total røykgass-strøm) ble testet. Resultatene viste at CO₂-konsentrasjonen i røykgassen minker med økende grad av falsk luft. Reduksjonen i CO₂-konsentrasjon fører til en økning av kraftbehovet for CO₂-reanseanlegget på ~2,6 % per prosent falsk luft, og CO₂-fangst-forholdet ble også redusert med økende mengde falsk luft. Disse resultatene stemmer bra med resultater fra tidligere oksy-forbrenning-studier, og viser viktigheten av å minimere luftinntrengning i sementanlegget ved bruk av CO₂-fangst ved oksy-forbrenning.

Dersom CO₂-fangst ved oksy-forbrenning skal brukes i et sementanlegg er det nødvendig med prosess-modifikasjoner og ekstra utstyr. En luft-separasjonsenhet (ASU) er nødvendig for å tilføre ren oksygen til forbrenningsprosessen. Et CO₂ kompresjons- og reanseanlegg (CPU) er også nødvendig for å kunne oppnå ønsket CO₂-renhet og for å tilfredsstille transportbetingelser.

Når oksy-forbrenningsteknologi brukes, vil både omformingen av materialene i sementbrennovnsystemet og operasjonsspesifikasjoner for den totale prosessen være forskjellig fra forholdene i en konvensjonell brennovn. Likevel viser forskning utført av ECRA i 2012 at de negative følgene av oksy-forbrenning på produktkvaliteten ser ut til å være neglisjerbare.

Andre nødvendige prosessmodifikasjoner når et anlegg skal oppgraderes med oksy-forbrenning er nytt design på klinkerbrennerene kjøleren i sementanlegget. I tillegg er det viktig å unngå unødvendig falsk luft ved å forbedre alle tetninger på anlegget, som simuleringsresultatene viser. Dette er mulig f.eks. ved bruk av avgass-skyllende systemer eller ved å forbedre vedlikehold av inspeksjonsdørene og lignende enheter. CPU-en er inntil en viss grad i stand til å håndtere endringer i røykgass-komposisjon ved korttidsinspeksjoner. Imidlertid vil dette begrense effektiviteten.

Table of Contents

Preface	i
Abstract	iii
Sammendrag	v
List of Figures	x
List of Tables	xi
Nomenclature	xii
Symbols	xii
Abbreviations and Acronyms	xiii
1 Introduction	1
1.1 Background.....	1
1.2 Objective.....	3
1.3 Limitations of Study	3
1.4 Approach	3
1.5 Structure of the Thesis	4
2 Cement Production	5
2.1 The Global Cement Industry	5
2.2 Cement Production Process and Plant Description	6
2.2.1 CO ₂ Emissions from Cement Production	7
2.2.2 Flue Gas Cleaning	8
2.3 The Norcem Cement Plant in Brevik, Norway.....	8
2.3.1 Current Kiln System at Norcem Brevik	9
3 Oxy-combustion CO₂ Capture in Cement Plants	13
3.1 Principle of Oxy-combustion.....	13
3.2 Integration of oxy-combustion into the cement plant technology	14
3.3 Air Separation.....	15
3.4 CO ₂ Compression and Purification Unit	18
3.4.1 Fundamentals of Compression	18
3.4.2 CO ₂ CPU Design.....	21
3.4.3 Requirements for CO ₂ Purity and Transportation	23
3.5 CO ₂ capture efficiency calculations	26

3.5.1	Theory of separation.....	26
3.5.2	Relating work requirement for CO ₂ capture and efficiency.....	27
3.5.3	CO ₂ avoided, CO ₂ captured and CO ₂ capture efficiency	28
3.6	Limits and Barriers for CCS in the Cement Industry	30
3.7	Technical Issues of Oxy-combustion in a Cement Plant.....	32
4	Process Simulation Model and Methodology.....	33
4.1	Simulation software.....	33
4.2	Fluid Property Packages in Aspen HYSYS.....	33
4.3	Existing Oxy-combustion Cement Process Configurations	34
4.3.1	IEA GHG Configuration 1	35
4.3.2	IEA GHG Configuration 2	36
4.3.3	IEA GHG Configuration 3	36
4.3.4	IEA GHG Configuration 4	37
4.3.5	ECRA Oxy-combustion Configuration.....	38
4.3.6	Jelmer de Winter's Oxy-combustion Layout	41
4.4	Chosen Oxy-Combustion Cement Plant Model in this Thesis	42
4.4.1	Overall Assumptions	43
4.4.2	Cement Model specifications	44
4.4.3	Heat Duties	46
4.4.4	CO ₂ from Calcination.....	46
4.4.5	Fuel Specifications and Characteristics.....	46
4.5	Oxy-combustion Specifications.....	47
4.5.1	Air Separation Unit (ASU).....	47
4.5.2	Specifications of the CO ₂ CPU	47
5	Simulation Results and Discussion	51
5.1	General.....	51
5.2	Flue gas CO ₂ concentration and CO ₂ purity.....	51
5.2.1	Effect of air in-leakage on the flue gas composition.....	51
5.2.2	Discussion and Comparison with previous studies	52
5.2.3	Product CO ₂ -purity.....	53
5.2.4	CO ₂ capture ratio.....	53

5.2.5	CO ₂ avoided	54
5.3	Additional Power Consumption with Oxy-combustion Capture.....	55
5.3.1	Power consumption, ASU	55
5.3.2	Power Consumption of CPU and ASU with different Air in-leakages.....	55
5.3.3	Comparison with previous studies	56
5.4	Conclusion, CPU design and air in-leakage	58
6	Cement Process Modifications and Operational Risks.....	59
6.1	General.....	59
6.2	Necessary Cement Process Modifications.....	59
6.2.1	Optimisation of sealing locations to reduce air in-leakage	59
6.2.2	Burner Design	63
6.2.3	Two-staged Clinker Cooler	63
6.3	Operational Risks	64
6.3.1	Impact of Oxy-combustion on Product Quality	64
6.3.2	Durability of refractory materials.....	65
7	Conclusions and Suggestions for Further Work	67
	References	69
	Appendices	71

List of Figures

Figure 1.1: Application of CCS in the cement sector; global deployment by region source (IEA, 2011).	2
Figure 2.1: World Cement Production 2012, by region and main countries. (CEMBUREAU, 2014) ..	5
Figure 2.2: Process Flow Diagram of a typical Cement Production Process.	6
Figure 2.3: Norway's Top 10 CO ₂ emissions in 2011 (Miljødirektoratet, 2012).	9
Figure 2.4: Kiln 6 system at Norcem Brevik (Tokheim, 2011).....	10
Figure 2.5: Current exhaust gas system on Kiln 6, Norcem Brevik (Tokheim, 2011).....	11
Figure 3.1: Oxy-combustion technology with flue gas recirculation (ECRA, 2009).....	14
Figure 3.2: Flow diagram of a cryogenic air separation unit (ECRA, 2009).	16
Figure 3.3: Power requirement of a cryogenic ASU (Darde et al., 2009).....	17
Figure 3.4: Simple Compression Process.	18
Figure 3.5: Multistage compression with intercooling.	20
Figure 3.6: p-h diagram of multistage compression with intercooling (Arora, 2010).	20
Figure 3.7: Specific energy consumption of different CPU schemes as a function of CO ₂ purity in the inlet flue gas. (Darde et al., 2009)	22
Figure 3.8: Specific energy consumption as a function of product pressure for 83 % inlet CO ₂ (dry basis) and no integration. (Darde et al., 2009)	23
Figure 3.9: Complete separation (left) and partial separation (right) of N gas components (Bolland, 2012).....	27
Figure 4.1: Oxy-combustion Cement Plant Configuration 1 – Diversion of preheater exit gases for fuel drying and subsequent capture and recycle (IEA, 2008).	35
Figure 4.2: 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 GHG, 2008).	36
Figure 4.3: Oxy-combustion Cement Plant Configuration 4 - Dual preheaters with oxy-combustion in the pre-calciner only (IEA, 2008).....	37
Figure 4.4: Oxy-combustion Plant Configuration 5 (ECRA, 2009).....	38
Figure 4.5: Jelmer de Winter's Oxy-combustion Layout.....	41
Figure 4.6: Oxy-combustion cement plant layout as modelled in this thesis.	42
Figure 4.7: Kiln and Calciner in HYSYS.	45
Figure 4.8: HYSYS CPU design.	48
Figure 4.9: Phase Diagram of CO ₂	49
Figure 5.1: Effect of air in-leakage on the dry flue gas composition.	51
Figure 5.2: Comparison of flue gas concentration from HYSYS model with ECRA (2012).	52
Figure 5.3: CO ₂ capture ratio at different air in-leakage rates.....	53
Figure 5.4: Comparison of CO ₂ capture ratio with ECRA (2012).	54
Figure 5.5: Comparison of CPU power consumption with ECRA (2012).....	57
Figure 5.6: Percentage increase in power consumption from CPU per percentage of air in-leakage. .	58
Figure 6.1: Proportional share in total false air ingress of the several sealing locations (ECRA, 2012).	60
Figure 6.2: Comparison of different scenarios for the reduction of false air ingress (ECRA, 2012)...	63

List of Tables

Table 2.1: Kiln Chemical Reactions (Adapted from IEA GHG, 2008)	7
Table 2.2: Typical flue gas composition in cement industry flue gas stream (Adina et al., 2009) ..	8
Table 3.1: Application areas and power consumption of oxygen supply systems (ECRA, 2009)	15
Table 3.2: Typical composition of streams for the oxy-combustion technology (Adapted from Bolland, 2012)	24
Table 3.3: CO ₂ quality requirements for transport and storage (Adapted from Bolland, 2012)	25
Table 4.1: Recommended Property Methods (Adapted from AspenTech, 2003)	33
Table 4.2: Application ranges for PR and SRK (Adapted from AspenTech, 2003)	34
Table 4.3: Comparison of the configurations for retrofitting and new built plants (ECRA, 2009)	40
Table 4.4: Coal and RDF Analysis (deWinter, 2013)	47
Table 5.1: CO ₂ in flue gas and product purity with different air in-leakage rates	53
Table 5.2: Results from sensitivity study	56
Table 6.1: Technical false air reduction potentials for the considered sealing location system (ECRA, 2012)	61

Nomenclature

Symbols

Latin letters

C_{CO_2}	Specific CO ₂ emissions	kg CO ₂ /kg clinker
C_e	Specific energy use	MJ _{LHV} /kg clinker
c_p	Specific heat capacity at constant pressure	kJ/kgK
c_v	Specific heat capacity at constant volume	kJ/kgK
h	Enthalpy	kJ/kg
k	Isentropic index	-
m	Mass	kg, tonnes
\dot{m}	Mass flow rate	kg/s, kg/h
M	Molecular weight	kg/kmol
n	Polytropic index	-
n	Number of moles	mole
p	Pressure	kPa, bar
P	Power	kW, MW
Q	Heat flow	kW
\dot{Q}	Heat flow rate	kWh, MJ
R	Gas constant	kJ/kmolK
T	Temperature	K, °C
v	Specific volume	m ³ /kg
\dot{W}	Work	kW
y	Molar fraction	mol %
Z	Compressibility factor	-

Greek letters

Δ	Differential	-
η	Efficiency	-
v	Specific volume	m ³ /kg
Φ	CO ₂ capture ratio	kg CO ₂ captured/kg CO ₂ formed
χ	CO ₂ emission index	kg CO ₂ /MJ _{fuel LHV}

Subscripts

c	Compressor
i	Component i of a gas
int	Internally
rev	Reversible
u	Universal

Abbreviations and Acronyms

ASU	Air Separation Unit
CAPEX	Capital Expenditures
CCS	Carbon Capture and Storage
CO	Carbon monoxide
CO ₂	Carbon dioxide
CPU	Compression and Purification Unit
ECRA	European Cement Research Academy
EOS	Equation of State
ESP	Electrostatic Precipitator
GHG	Greenhouse Gas
GSA	Gas Suspension Absorber
HP	High Pressure
IEA	International Energy Agency
kWh	Kilo Watt hours
LHV	Lower Heating Value
LP	Low Pressure
MSW	Municipal Solid Waste
MW	Mega Watts
NO _x	Nitrogen Oxides
O ₂	Oxygen
OPEX	Operational Expenditures
PFD	Process Flow Diagram
ppm	Parts per million
PR	Peng-Robinson
PRSV	Peng-Robinson-Stryjek-Vera
PSA	Pressure Swing Adsorption
RDF	Refused Derived Fuels
RM	Raw Mill
SO _x	Sulphur oxides
SRK	Soave-Redlich-Kwong
tpd	Tonnes per day
tph	Tonnes per hour
UNIDO	The United Nations Industrial Development Organization
VPSA	Vacuum Pressure Swing Adsorption
VSA	Vacuum Swing Adsorption

1 Introduction

1.1 Background

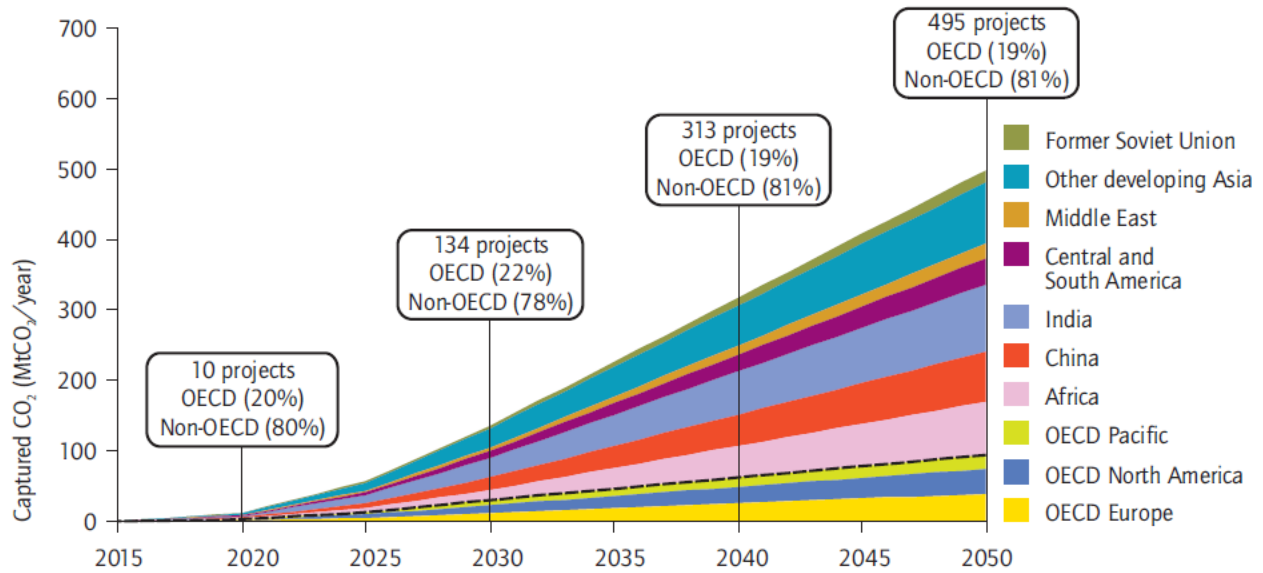
Cement is the essential component in concrete, a fundamental building material for society's infrastructure around the world. Concrete is second only to water in total volumes consumed annually by society. But the production of cement also co-produces CO₂, causing the cement industry to produce approximately 5-7 % of current global man-made CO₂ emissions. In 2006, the cement industry emitted 1.88 Gt of CO₂ (IEA, 2009). The cement production is forecast to grow further, in particular in developing countries.

Global production of cement has grown steadily over many years, reaching 2,500 million tonnes in 2006. (IEA GHG, 2008) The main growth has been in Asia, in particular in China. China now accounts for around 60 % of all global cement production.

Over the years, the cement industry has substantially reduced emissions of CO₂ per tonne of cement by improving energy efficiency, replacing fossil fuels with wastes, and by increasing the use of additives in the cement product. At present, CO₂ capture and storage (CCS) represents one of the few opportunities to further reduce CO₂ emissions from cement production, and the industry is currently considering the feasibility of applying this technique in order to plan for the future. The cement industry represents a good opportunity for CCS, because cement plants are relatively large point sources of CO₂, the CO₂ concentration in cement plant flue gas is relatively high (about 25 mol-%, dry basis) and over 60 % of the total CO₂ emissions from a modern cement plant are from mineral decomposition, which cannot be avoided by use of alternative energy sources. (IEA GHG, 2008)

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

In 2011, the United Nations Industrial Development Organization (UNIDO) in cooperation with the IEA published a new roadmap on CCS in industrial applications [IEA, 2011]. According to this roadmap, to reach the results of the 2010 BLUE Map Scenario (a 50 % reduction in CO₂ emissions from the 2005 levels by 2050), the cement industry is seen to have the potential to capture 500 Mt CO₂/year in 2050 by the application of CCS technologies, see Figure 1.1.



Note: The dashed line indicates separation of OECD/non-OECD groupings.
Source: IEA analysis.

Figure 1.1: Application of CCS in the cement sector; global deployment by region source (IEA, 2011).

While the overall technical feasibility is still open, it is already obvious that the estimated costs for CCS application in the cement industry will be extremely high. From today's view, cement production costs would roughly double (ECRA, 2012).

The three main CO₂ capture technologies available today are:

- Post-combustion capture, where CO₂ is separated from the flue gas.
- Pre-combustion capture, in which fuel is reacted with oxygen and steam to produce a mixture of CO₂ and H₂. The CO₂ is then separated from the H₂, and the H₂ is used as fuel.
- Oxy-combustion capture, where fuel is burnt with oxygen instead of air, to produce a flue gas consisting mainly of CO₂.

Post-combustion and oxy-combustion capture are the most relevant technologies for CCS in the cement industry, as pre-combustion would only be able to capture the fuel-derived CO₂, not the larger quantity of CO₂ originating from the decomposition of limestone (CaCO₃) into CaO.

This thesis will focus on oxy-combustion CO₂ capture. The work is related to the NORDICCS project where the potential of CCS in the Nordic region is investigated.

1.2 Objective

The objectives of the thesis work have been to model and simulate oxy-combustion CO₂ capture in a cement plant. The process simulation tool Aspen HYSYS was used to make a steady-state process model. A starting point for the process modelling was Jelmer de Winter's project work from 2013. In addition to the process simulation, an engineering evaluation of the necessary modifications to the cement process was conducted.

The following tasks were considered:

1. Review of literature related to oxy-combustion CO₂ capture and cement production.
2. Process simulation of the calcination process with varying degree of air in-leakage, where the heat is supplied by combustion in oxygen followed by capture of the CO₂.
3. Evaluate further gas separation after H₂O condensation to achieve the required CO₂ quality.
4. Evaluation of necessary cement process modifications and analysis of operational risks due to the modifications.

1.3 Limitations of Study

The cryogenic ASU includes somewhat complicated unit operators and is complicated to model in HYSYS, and construction of an accurate simulation model by the use of HYSYS is seen to be too time consuming for this thesis work. A simulation model of the ASU is thus not constructed, after agreement with my supervisors Post.doc. Lars Nord and Post.doc. Chao Fu.

An economic evaluation of the oxy-combustion technology has not been conducted, as it is beyond the scope of this thesis.

1.4 Approach

This thesis is based on the following main sources of information:

- A review of published literature
- Jelmer de Winters Project Thesis from December 2013
- Process simulation using Aspen HYSYS
- Discussions with supervisors

1.5 Structure of the Thesis

The report is organized in 7 chapters, including this introduction.

Chapter 2 – Cement Production gives an introduction to the global cement industry and basic description of the cement production process. It also describes the technology used at the Norcem cement plant in Brevik, Norway.

Chapter 3 – Oxy-combustion CO₂ Capture in Cement Plants describes the principle of oxy-combustion, and the integration of oxy-combustion CO₂ capture in cement production. The Air Separation Unit (ASU) and CO₂ compression and purification unit (CPU) are described. In addition, basic theory about compression and separation and equations used in CO₂ capture calculations are presented, and limits and barriers for CCS and technical issues of oxy-combustion are elaborated.

Chapter 4 – Process Simulation Model and Methodology deals with the process simulation model and methodology used in this study, including existing oxy-combustion process models. Further gas separation after H₂O condensation to achieve required CO₂ quality is evaluated.

Chapter 5 – Simulation Results and Discussion presents the results obtained by the HYSYS simulation model, and the results are further discussed and compared with previous studies.

Chapter 6 – Necessary Cement Process Modifications and Operational Risks contains an evaluation of necessary cement process modifications and operational risks due to these modifications.

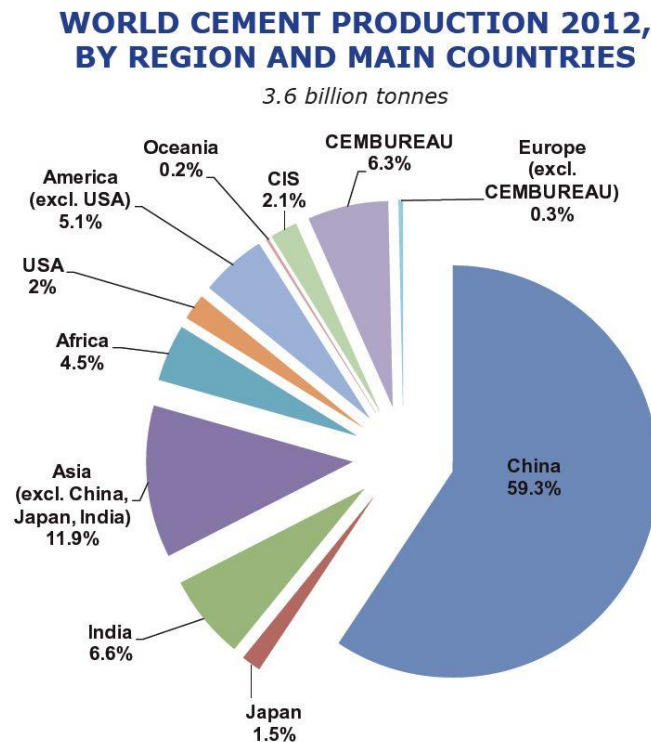
Chapter 7 is the conclusion of the thesis, and suggestions for further work are given.

2 Cement Production

2.1 The Global Cement Industry

Cement production is an energy intensive production process, accounting for 2 % of the global primary energy consumption (Worrell et al., 2001) and between 6-7% of global industrial energy use (IEA, 2007). Its reliance on carbon intensive fuels such as coal and petroleum coke in the clinker making process causes substantial CO₂ emissions directly from the combustion of fossil fuels. CO₂ is also emitted from the calcination process of limestone into calcium oxide and from the consumption of electricity generated from fossil fuels. The cement industry is one of the world's largest industrial sources of CO₂ emissions. Approximately 5 % of global anthropogenic carbon dioxide emissions result from the manufacture of cement, with nearly 0.7-1.1 tonne of CO₂ being emitted for every tonne of cement produced. (Bosaga et al., 2009) In 2006, the cement production accounted for 1.88 Gt/year of CO₂ emissions worldwide. (IEA, 2009)

Figure 2.1 shows the world cement production in 2012. The largest cement producer, by far, is China, who accounted for almost 60 % of the world's cement production in 2012, producing more than 2 billion tonnes of cement.



† IMF World Economic Outlook 2013, April 2013

Figure 2.1: World Cement Production 2012, by region and main countries. (CEMBUREAU, 2014)

2.2 Cement Production Process and Plant Description

Cement is composed of calcium silicates, calcium aluminates and calcium aluminoferrite minerals. It is produced from a mixture of raw materials, principally calcium carbonate. The most common type of cement in general use around the world is called Portland cement. Typical production capacity for a modern European cement plant is 1 Mt/year of cement.

The general cement production process is illustrated in Figure 2.2. The raw materials are ground together into a fine powder and delivered to a cement kiln. In the kiln the raw materials react together at high temperature to form an intermediate ‘clinker’, which is ground together with some gypsum and other additives to form cement. Historically clinker production has evolved from wet processes in which raw materials are ground in water, through semi-wet and semi-dry processes to dry processes, in which the raw materials are dried and ground before feeding to preheaters and a kiln. The dry process requires less energy than the wet process and thus is generally favoured where its application is feasible. In industrialised countries rotary kilns are used, which can have production capacities of up to 10,000 tonnes clinker per day. (IEA GHG, 2008)

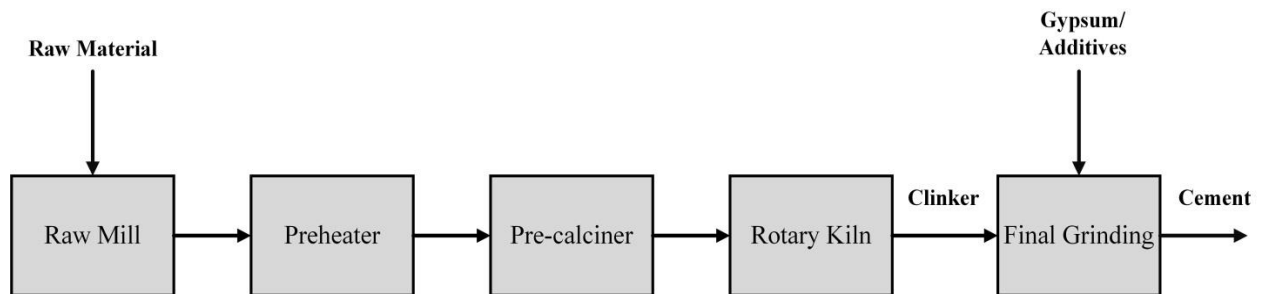


Figure 2.2: Process Flow Diagram of a typical Cement Production Process.

In both the pre-calciner and the cement kiln, calcium oxide (CaO) is produced from the calcination process of limestone (CaCO₃). An additional product of this reaction is CO₂.



The CaO is further used together with silica (SiO₂), iron oxide (Fe₂O₃) and alumina (Al₂O₃) to form the cement clinker.

The kiln system, consisting of drying and preheating, the pre-calciner, the rotary kiln and the clinker cooler, involves several successive chemical reactions taking place as the temperature of the raw mix rises. The reaction stages are shown in Table 2.1.

Table 2.1: Kiln Chemical Reactions (Adapted from IEA GHG, 2008)

Kiln temperature (°C)	Chemical Reaction
20 – 900	Drying and Preheating: the release of free and chemically bound water
850 – 950	Calcination: the release of CO ₂ from calcium carbonate (limestone) and initial reactions with formation of clinker minerals and intermediate phases
1250 – 1450	Sintering or clinkerisation: the formation of calcium silicates and partial melting
1350 – 1200	Kiln internal cooling: crystallisation of calcium aluminate and calcium ferrite from the partial melt

Typically, a peak temperature of 1400-1450 °C is required to complete the reactions and produce alite, the characteristic constituent of Portland cement. Partial melting causes the material to aggregate into lumps or nodules known as clinker, which is then cooled down with air to 100-200 °C. Waste heat from the kiln system is generally used for drying the raw materials in the grinding section of the production process.

2.2.1 CO₂ Emissions from Cement Production

In a modern cement plant, CO₂ is emitted as follows:

- 60 % of the CO₂ results from the calcination of limestone (CaCO₃) into CaO and CO₂
- 30 % from combustion of fuels in the kiln
- 10 % from other downstream plant operations.

Thus, measures like energy efficiency improvements (use of energy efficient equipment, replacement of old installations, process modifications etc.), fuel switching to waste as alternative fuel, and cement blending using industrial by-products, can only help decrease the CO₂ emissions associated with energy conversion. (Vatopoulos & Tzimas, 2012)

Significant overall emission reduction can only be achieved with the application of carbon capture and storage (CCS) technologies. Cement plant flue gas has a relatively high CO₂ concentration; typically around 14-33 %, compared to 12-14 % CO₂ for coal-fired power plants and 4 % CO₂ for gas-fired power plants, and therefore represents a better opportunity for implementing CCS, especially when compared to gas-fired power plants.

2.2.2 Flue Gas Cleaning

Typical flue gas composition in cement industry flue gas streams are given in Table 2.2:

Table 2.2: Typical flue gas composition in cement industry flue gas stream (Adina et al., 2009)

Component	Concentration
CO ₂	14 – 33 % (w/w)
NO ₂	5 – 10 % of NO _x
NO _x	<200-3000 mg/Nm ³
SO ₂	<10-3500 mg/Nm ³
O ₂	8 – 14 % (v/v)

Emissions of NO_x and SO_x are regulated, and removal is necessary to comply with these regulations. Industrial plants are usually equipped with either Electrostatic Precipitators (ESPs) or fabric filters to remove particulates. Both ESPs and fabric filters are very efficient at removing particulates, and remove more than 99.9 % of particulates (by mass). As a result, flue gas out of the cement plant will mainly consist of CO₂, nitrogen, oxygen, argon and water vapour.

2.3 The Norcem Cement Plant in Brevik, Norway

The HeidelbergCement Group subsidiary Norcem is the only cement producer in Norway, and has plants in Brevik in southern Norway, and Kjøpsvik in the northern Norway. About 70 % of the total cement production is at the Brevik plant. The Norcem plants are among the most modern cement plants in Europe, also when considering energy use and emission reductions. Yearly production capacity at the Brevik plant is approximately 1.05 million tonnes of clinker and 1.3 million tonnes of cement. Assuming 350 days of operation per year, this corresponds to 3,000 tonnes clinker per day.

Figure 2.3 shows Norway's top ten CO₂ emissions in 2011. The green dots indicate sources where there have been reductions in emissions since 2010, while the red dots indicate an increase in emissions since 2010. Norcem Brevik is the only company among the top ten largest industrial emission sources that is not in the oil and gas industry.

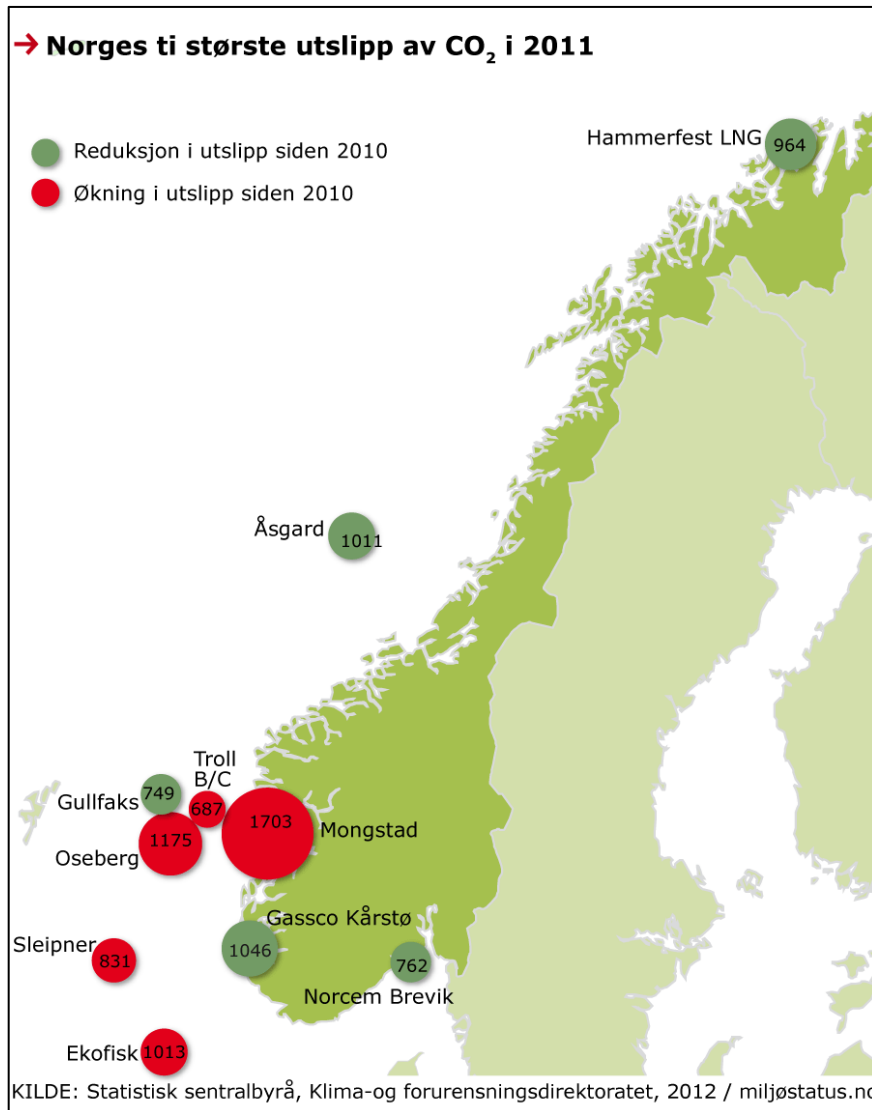


Figure 2.3: Norway's Top 10 CO₂ emissions in 2011 (Miljødirektoratet, 2012).

The total CO₂ emissions from the Norcem plant are assumed to be approximately 900,000 tonnes CO₂/yr (corresponding to around 120 tCO₂/hr). (Tokheim, 2011)

2.3.1 Current Kiln System at Norcem Brevik

A sketch of the current kiln system at Norcem Brevik is given in Figure 2.4, and a simplified block diagram of the exhaust gas system is shown in Figure 2.5. The rotary kiln produces three types of clinker, and seven types of cement are manufactured in three cement mills.

The kiln process is characterized by a flue gas stream divided over two strings after the pre-calciner. Both strings are fed through a series of cyclone preheaters (PH1 and PH2) and cooled down by condensing towers (CT1 and CT2). The exhaust gas is dedusted in the electrostatic precipitators (ESP4 in string 1 and ESP3 in string 2). (Tokheim, 2011)

A Gas Suspension Absorber (GSA) system, which removes SO_x , was installed on string 1 in 2010. The GSA causes the exhaust gas characteristics after the fabric filter (bag filter) on string 1 (FF1) to be different from string 2 when the GSA is in operation, in terms of temperature, pressure, moisture and SO_x content. Because of this, CO_2 and O_2 concentrations in string 2 compared to string 1 will also be different.

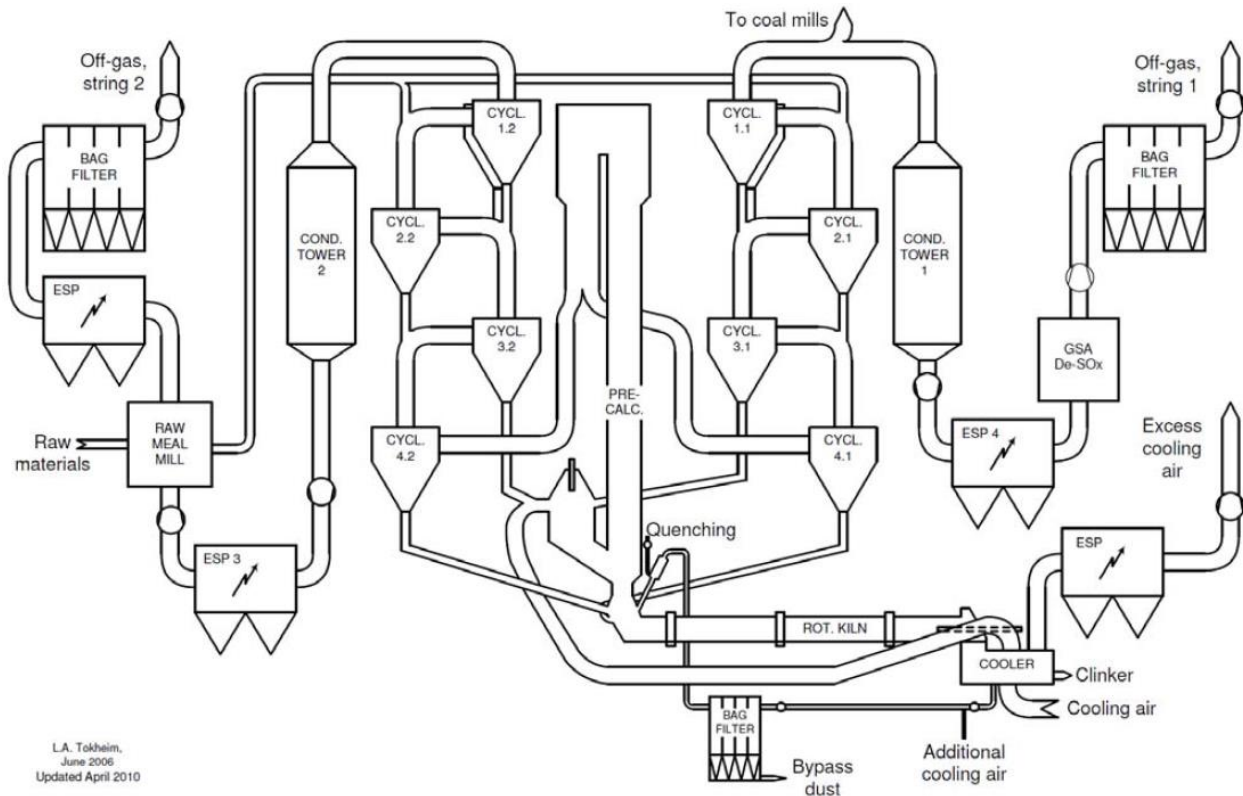


Figure 2.4: Kiln 6 system at Norcem Brevik (Tokheim, 2011).

The exhaust gas in string 2 is routed to the raw mill department, where part of the thermal energy in the exhaust is used for drying of raw materials in the raw mill (RM). This causes the temperature after CT2 to (usually) be higher than the temperature after CT1. After dust removal the exhaust gas in string 2 is released to the surroundings. There is false air in-leakage in both strings, in particular in the raw meal (RM) department in string 2.

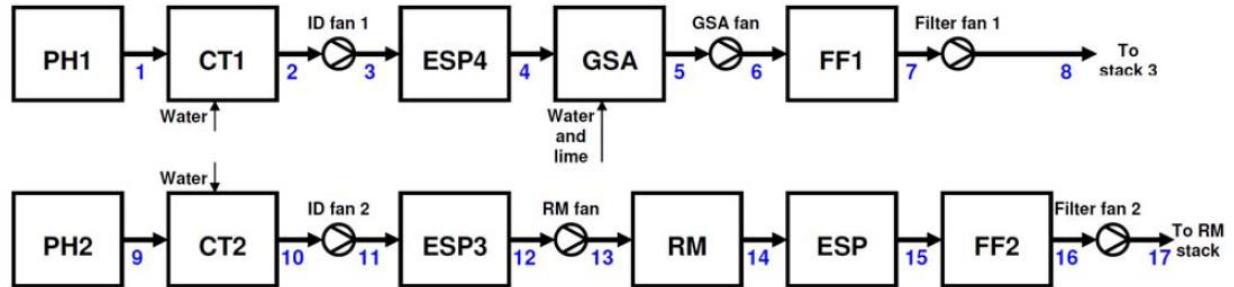


Figure 2.5: Current exhaust gas system on Kiln 6, Norcem Brevik (Tokheim, 2011). The blue numbers refer to stream names from Tokheim and are not further described here.

It is currently not made any decision to what percentage of the exhaust gas that will be cleaned. This means that it is also not resolved whether the exhaust gas from both strings will be cleaned; cleaning only one of them (preferably string 1) will be significantly more cost-effective, as CO₂ capture on string 2 exhaust would require installation of a de-SO_x unit (GSA) on that string. Without the GSA installed on string 2, CO₂ capture on that string might be excluded due to too high SO₂ concentrations.

3 Oxy-combustion CO₂ Capture in Cement Plants

3.1 Principle of Oxy-combustion

The technology of oxy-combustion has been applied for example for power generation and in the glass and the steel sector, so far however mainly aiming to increase the efficiency of the burning process (ECRA, 2012). Its application for CO₂-emission reduction has been investigated predominantly by the energy sector during the past years.

In oxy-combustion (or oxyfuel) CO₂ capture, the combustion process takes place with pure or almost pure oxygen and with close to zero oxygen excess. The use of oxygen in pure form avoids the combustion products being diluted with nitrogen, and the flue gas generated will mainly consist of CO₂ and H₂O. The subsequent purification of CO₂ is achieved by cooling of the flue gas and condensing the water vapour (Bolland, 2012).

Combustion with pure oxygen results in an excessively high flame temperature. Flame temperatures in excess of 3500 °C can typically be achieved, which is too hot for normal operation of a cement plant. To amend this, CO₂ and/or H₂O rich flue gas can be recirculated to the combustor to moderate the temperature. The flame temperature can be adjusted by changing the flue gas recirculation rate.

However, due to the requirements for high temperatures (up to 1450 °C) to achieve calcination and clinker formation, the fact that it is far easier to reach high temperatures in oxygen combustion compared to air combustion could be seen as an advantage for operating the cement process, as it may lead to shorter residence times and permit reductions in size. (IEA GHG, 2008)

Oxygen is usually produced by low temperature (cryogenic) air separation in an air separation unit (ASU), which is the standard technology today for large-scale production of oxygen. For industrial applications such as cement production, the oxygen purity is usually 90-95 %. The nitrogen is removed in a separation plant (ASU) from the air prior to being applied to the kiln and pre-calciner. Consequently, the concentration of carbon dioxide in the flue gas increases 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 combustion with ambient air. To maintain an appropriate flame temperature, part of the flue gas has to be recycled, as described above. Figure 3.1 shows the oxy-combustion process with recirculating flue gas.

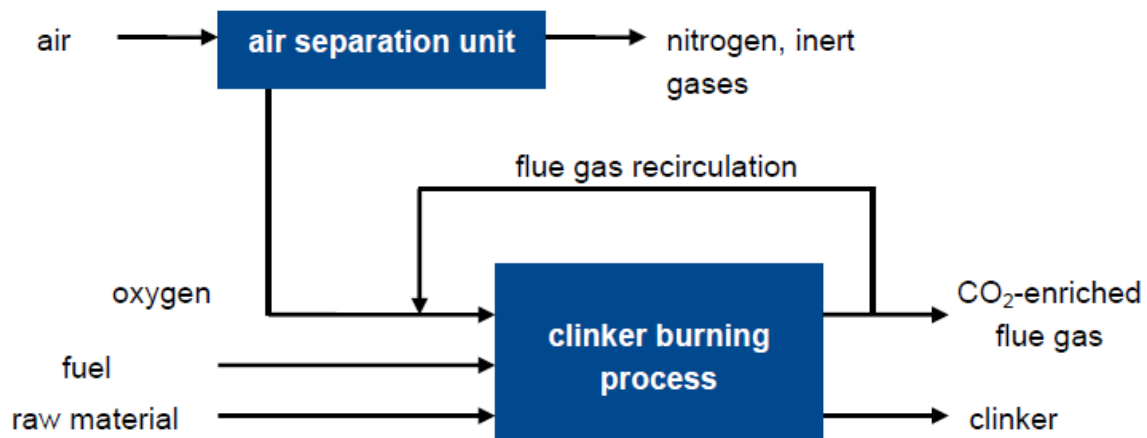


Figure 3.1: Oxy-combustion technology with flue gas recirculation (ECRA, 2009).

Oxy-combustion technology at a cement plant will cause a high CO₂ concentration in the flue gas (above 80 mol%). The high concentration flue gas is then purified to 95 % CO₂ in a relatively simple cryogenic separation unit during compression. (IEA GHG, 2008) Higher purities can be achieved if necessary by employing cryogenic distillation, however at a higher energy cost.

3.2 Integration of oxy-combustion into the cement plant technology

Implementation of oxy-combustion CO₂ capture at a cement plant requires the following additional equipment:

- Air Separation Unit (ASU) for production of high-purity oxygen
- CO₂ Compression and Purification Unit (CPU) to purify the exhaust gas and compress the CO₂ to required CO₂ quality and pressure (usually 95 % CO₂ at 110 bar).
- Recirculation pipe to recirculate some of the exhaust gas back to the kiln to avoid too high temperatures in the kiln, i.e. to keep the temperature in the kiln at maximum 1450 °C.

Oxy-combustion CO₂ capture causes significant auxiliary power consumption, compared to normal operation without CO₂ capture. The compressor work in the ASU and the CO₂ CPU are the main causes of the increased power consumption. Reducing the CO₂ compression work is therefore an important parameter in commercializing oxy-combustion CO₂ capture.

In addition, process modifications to the cement plants, particularly the kiln burners and the cooler, might be necessary. An evaluation of necessary cement process modifications are found in Chapter 5.

3.3 Air Separation

In order to provide the required oxygen purity in the oxy-combustion technology, oxygen has to be produced by air separation in an Air Separation Unit (ASU). The standard technology for large-scale production of oxygen is cryogenic separation.

ASUs based on cryogenic distillation have a very high reliability of over 99 % and an overall time availability of over 98 %. Every 3-4 years the ASU has to be shut down for defrosting and cleaning for about a 10 day period. (Bolland, 2012)

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 (ECRA, 2009). The oxidizer is produced by the separation of air. Air consists mainly of nitrogen, oxygen, argon and small amounts of carbon dioxide. The separation technologies are based either on differences in boiling points, different molecular weights or other properties of the components. The commercially available separation techniques are cryogenic distillation and non-cryogenic methods, which are using membranes or adsorbents to remove unwanted components. The range of purity, capacity and power consumption of the different separation systems are shown in Table 3.1.

Table 3.1: Application areas and power consumption of oxygen supply systems (ECRA, 2009)

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, cryogenic air separation is currently the most power efficient technology for the production of large quantities of oxygen. The system relies on the different boiling point temperatures of oxygen (-182.9 °C) and nitrogen (-195.8 °C), and can separate air into its elemental components in liquid form at temperatures around -185 °C. Beside oxygen production high-purity nitrogen and argon can be produced as by-products at relatively low additional costs.

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 the flow diagram in Figure 3.2. 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. This is essential to avoid freezing and deposits on the surface

within the process equipment at the very low temperatures. Two basic possibilities exist for the purification: the molecular sieve and reversing exchangers. The molecular sieves remove the impurities by adsorption, while the reversing exchanger makes them freeze out on the wall. 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 a 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 pressure (HP) and low pressure (LP) column. The low pressure is operated slightly above atmospheric pressure, while the high pressure column has a pressure around 4-7 bar. 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 (-185.9 °C) and will preferably stay in the product. If high purity oxygen is required, more distillation stages and removal of argon from a point in the lower pressure column where its concentration is highest are necessary. (ECRA, 2009)

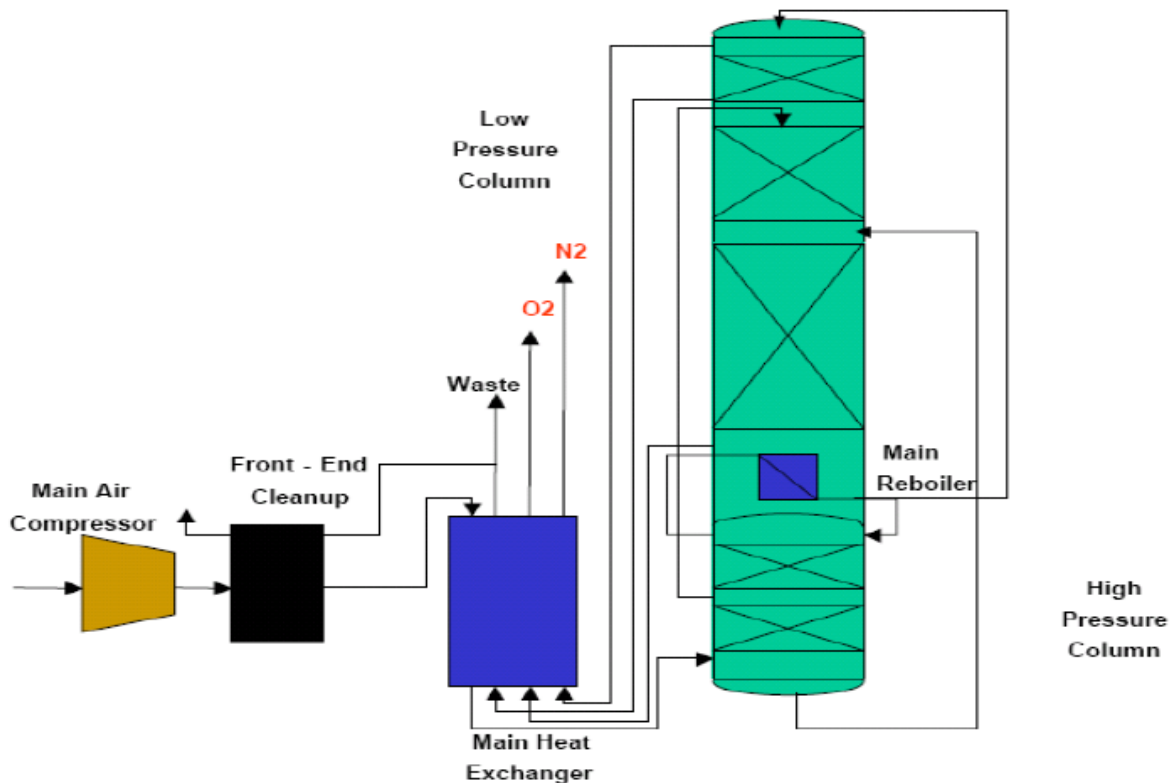


Figure 3.2: Flow diagram of a cryogenic air separation unit (ECRA, 2009).

The cryogenic air separation unit can produce oxygen with purities up to 99 vol.-%. However, increasing the oxygen purity significantly increases the energy demand. Figure 3.3 displays the energy of separation as a function of the oxygen purity in a cryogenic ASU.

Energy of separation is defined as:

- The power required to produce 1 metric ton of gaseous oxygen at a given oxygen purity at atmospheric pressure under ISO conditions (15 °C, 60 % relative humidity).

The efficiency of the compressor motors, heat of regeneration of driers and power consumption of the cooling system are not considered in this definition (Darde et al., 2009).

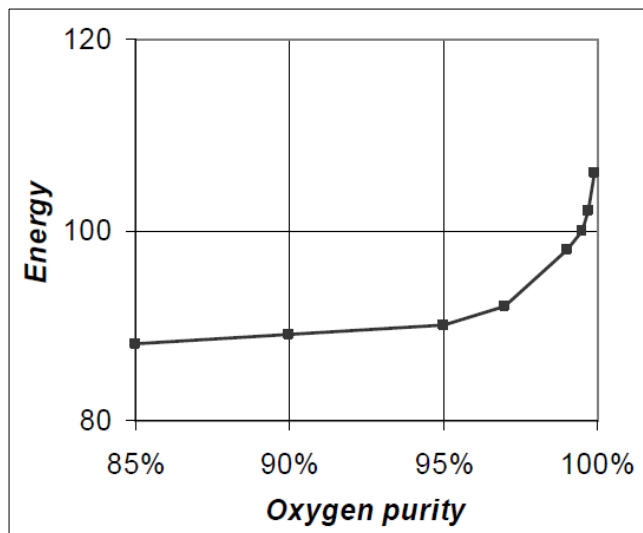


Figure 3.3: Power requirement of a cryogenic ASU (Darde et al., 2009).

As can be seen from Figure 3.3, the energy of separation rises almost linearly until 97 vol.-%, where the energy of separation required increases significantly. This is because the separation changes from oxygen-nitrogen to oxygen-argon in the LP column. Since the differences in boiling points of oxygen and argon are small, the power consumption rises. Although higher oxygen purity enhances the subsequent CO₂ purification, the operating costs as well as capital costs of the ASU are substantially increased. Therefore the optimum purity has been found to be between 95 and 97.5 vol-% (ECRA, 2009).

A study performed by Fu Chao at NTNU shows that specific energy consumption of producing oxygen with a cryogenic ASU on average is 0.198 kWh/kgO₂ for 95 % oxygen purity. This is assumed to be a reasonable value for commercial ASUs. (Chao Fu, Personal communication, February 2014)

3.4 CO₂ Compression and Purification Unit

In oxy-combustion, the resulting CO₂ stream usually contains between 80 % and 90 % CO₂, and is not of the necessary storage quality. In order to achieve the necessary CO₂ content - usually 95 % - a CO₂ purification step is required. Flue gas liquefaction or physical separation by compression-liquefaction is the most economical solution for the further CO₂ purification (Vatopoulos and Tzimas, 2012). The energy consumption is strongly affected by the air in-leakage, where a 4.5 % increase in energy consumption has been reported for every 1 % increase in air in-leakage (ECRA, 2009). The figures from ECRA are compared to simulation results from this thesis in Chapter 6.

The CPU is the main cause of the increased power consumption when implementing the oxy-combustion CO₂ capture technology, and reducing the CO₂ compression work is thus an important parameter when commercializing the technology. In the following, the fundamentals of compression are presented and the design parameters of the CPU discussed.

3.4.1 Fundamentals of Compression

Both the ASU and the CPU consists of compressors, and a thermodynamic understanding of compression is thus important and presented below.

One-stage compression

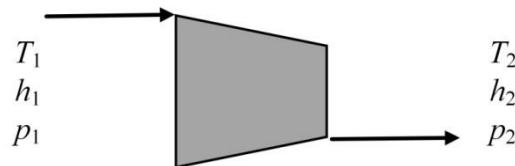


Figure 3.4: Simple Compression Process.

Figure 3.4 illustrates a simple compression process. For a reversible compressor, neglecting changes in mechanical potential and kinetic energy, compression work can be expressed as (Moran and Shapiro, 2010):

$$\left(\frac{\dot{W}_c}{\dot{m}}\right)_{int, rev} = \int_{p_1}^{p_2} v dp, \quad (3.1)$$

where \dot{m} is the mass flow rate [kg/s], \dot{W}_c is the compressor work [kW] and v is the specific volume [m³/kg]. For a polytropic compression (i.e. a real compression), the relationship between pressure and specific volume is $pv^n = constant$, where n is the polytropic index. Substituting this into (3.1) and performing the integration, gives the relation:

$$\dot{W} = Z_1 * \frac{nRT_1}{n-1} \left[\left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right], \quad (3.2)$$

where Z is the compressibility factor, n is the polytropic index, T_1 is the compressor inlet temperature, p_1 [kPa] is the inlet pressure and p_2 is the outlet pressure. R [kJ/kgK] is the gas constant, expressed as the ratio between the universal gas constant R_0 (8.314 kJ/kmolK) and the molecular weight M [kg/kmol].

The inlet temperature T_1 plays an important role for the magnitude of compression work. The temperature ratio can be expressed in terms of the pressure:

$$\frac{T_2}{T_1} = \left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} \quad (3.3)$$

where n can be calculated from:

$$n = \frac{\eta_p}{\eta_p - \frac{k-1}{k}}. \quad (3.4)$$

η_p is the polytropic efficiency for the compressor and k is the isentropic index, which is given by the ratio of the heat capacity at constant pressure (c_p) and the heat capacity at constant volume (c_v).

From Equations (3.2) and (3.3) it can be seen that a low inlet temperature will decrease the compressor work, if the pressure ratio is fixed. Equations (3.2) and (3.4) show that for constant polytropic efficiency, a high k -value results in lower power consumption for the same pressure ratio. The compressor work is also affected by the molecular weight of the gas, as the compression work \dot{W} is a function of the gas constant. A high molecular weight will result in a lower R -value, and thus the specific work will decrease.

Multi-stage compression

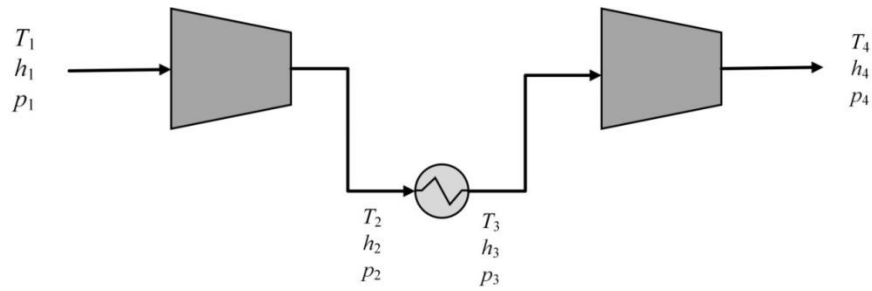


Figure 3.5: Multistage compression with intercooling.

Multistage compression with intercooling is utilized in order to minimize compression work. Figure 3.5 illustrates the principle of multistage compression intercooling. The compression is split into two or more stages with a cooler in-between the stages. The work of an intercooled compression as shown in Figure 3.5 can be calculated as:

$$\dot{W} = \dot{m} * \frac{nR}{n - 1} \left[T_1 \left(\left(\frac{p_2}{p_1} \right)^{\frac{n-1}{n}} - 1 \right) + T_3 \left(\left(\frac{p_4}{p_3} \right)^{\frac{n-1}{n}} - 1 \right) \right] \quad (3.5)$$

Since $p_2 \approx p_3$ and $T_2 > T_3$, it follows that the total compression work will be less for an intercooled compressor than for a compression without intercooling as long as the total pressure ratio of the compressor is the same. The decrease in compression work is represented by the shaded area in Figure 3.6.

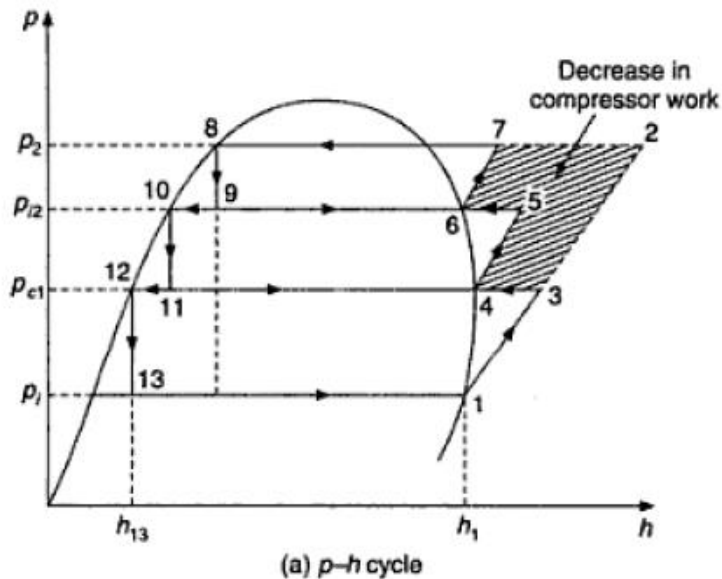


Figure 3.6: p-h diagram of multistage compression with intercooling (Arora, 2010).

Figure 3.6 illustrates the effect of multistage compression with intercooling for an isentropic compressor. For a one stage compressor with pressure ratio p_2/p_1 the total enthalpy increase is $h_2 - h_1$. If the gas is compressed in three stages, and cooled near its saturation line between each stage, the compression work will decrease as seen from the graph above. The total enthalpy increase can then be expressed as $(h_7 - h_6) + (h_5 - h_4) + (h_3 - h_1)$.

3.4.2 CO₂ CPU Design

The purpose of the CO₂ CPU is to capture CO₂ from combustion flue gases and purify it to the required specifications. Thus, both the composition of flue gases and CO₂ product specifications have a strong influence on the design and cost of the CO₂ CPU.

In the CPU, the flue gas is compressed, and most of the water is condensed out, before the CO₂ is purified and pumped to the required pressure. To reduce the overall power consumption, a combination of compression, condensation and pumping is used. The most common CO₂ CPU configuration is to compress the gas in several stages with intercooling. The gas is cooled and water is removed between each compression stage. Water needs to be removed in several stages because the solubility of water in CO₂ decreases with pressure.

Several different CO₂ CPU configurations exist. The choice of configuration is dependent on the flue gas composition, desired CO₂ recovery rate, product specifications and the trade-off between capital expenses (CAPEX) and operating expenses (OPEX). There exist three main CO₂ CPU schemes [Darde et al., 2009]:

- 1. No purification.** If 100 % CO₂ recovery rate is required, the CPU can be designed with *no purification*. In this scheme, the flue gas purification step is skipped. Thus, the entire flue gas is compressed, dried and compressed again, and then pumped to its final pressure. However, the CO₂ purity of this product is quite similar to that in the flue gas, on a dry basis. This scheme is therefore useful only for plants where the flue gas purity is quite close to the desired product purity. The scheme does not target to reduce any other gas components, and thus cannot meet any specifications on minor components in the product stream, and will typically deliver a product with O₂ in the single percentage range.
- 2. Partial condensation in a cold box.** Here, the compressed and dried flue gas is cooled to a very low temperature to condense out at least 90 % of the CO₂. CO₂ purity in the condensed phase is a function of the pressure and composition of the inlet gas to the partial condenser system, the number of stages of partial condensation in the cold box and the condensation temperature(s). 95 % CO₂ purity is usually achieved quite easily for typical flue gas compositions. This scheme can deliver a product with O₂ in the thousands of ppm range.

- 3. Cold box including distillation**, or cryogenic distillation. This is an extension of case 2 in which a distillation column is used to further purify the condensed CO₂ stream in the cold box. This scheme does also target 90 % CO₂ recovery, and a CO₂ purity in excess of 99 % can be achieved. The distillation column also helps to reduce the O₂ content to the low ppm range.

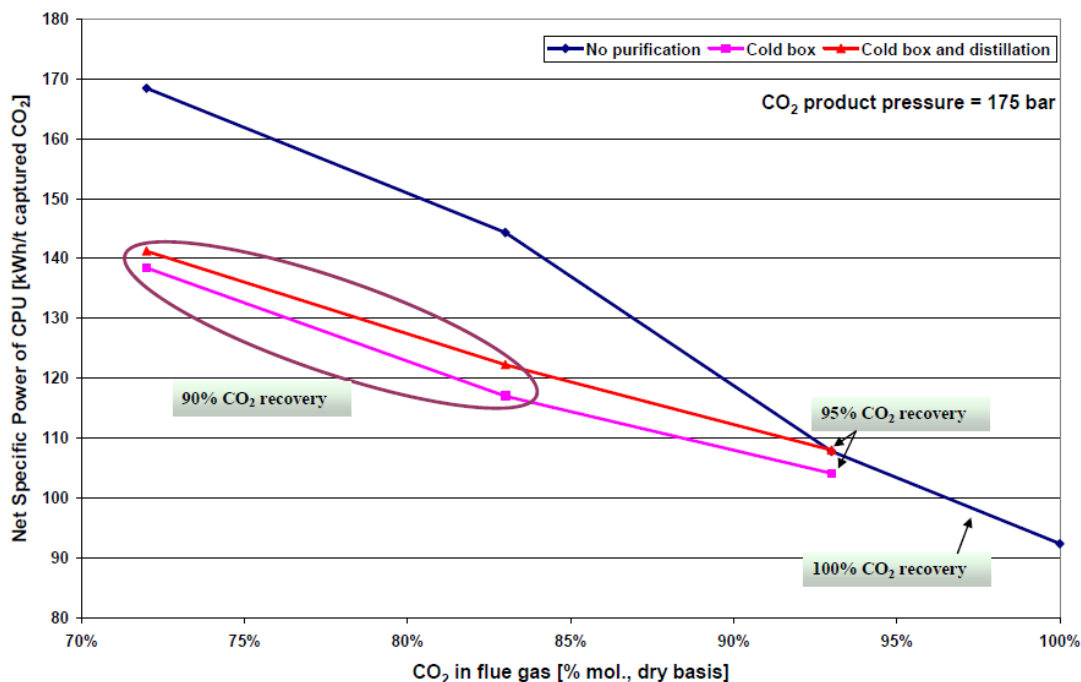


Figure 3.7: Specific energy consumption of different CPU schemes as a function of CO₂ purity in the inlet flue gas. (Darde et al., 2009)

Figure 3.7 shows the specific power consumption of the above schemes as a function of flue gas composition for a CO₂ product pressure of 175 bar. It can be seen that the power requirement of the CPU unit decreases with increasing CO₂ content. This is because a lower volume of total gas has to be compressed and treated to capture the same quantity of CO₂. At the interception between the red and the blue graph (~ 93 %), the different schemes require almost the same amount of energy, but with a 5 % difference in recovery rates. For CO₂ content of less than ~ 93 %, it can be seen from the figure that the cold box configuration with or without distillation requires significantly less energy to meet product specifications than the no purification scheme.

The graphs in Figure 3.7 are based on pulverized coal combustion and a CO₂ product pressure of 175 bar, but the energy consumption is expected to be similar for a CPU installed at a cement plant at similar CO₂ inlet concentrations and product pressure. The overall power requirement of the CPU is dependent of the product pressure. Darde et al. (2009) ran simulations with different product pressures. Figure 3.8 shows the specific energy consumption as a function of product pressure for an inlet CO₂ of 83 %. It can be seen that flue gas purification in a cold box requires

significantly less specific energy than no purification for the entire range of product pressures studied.

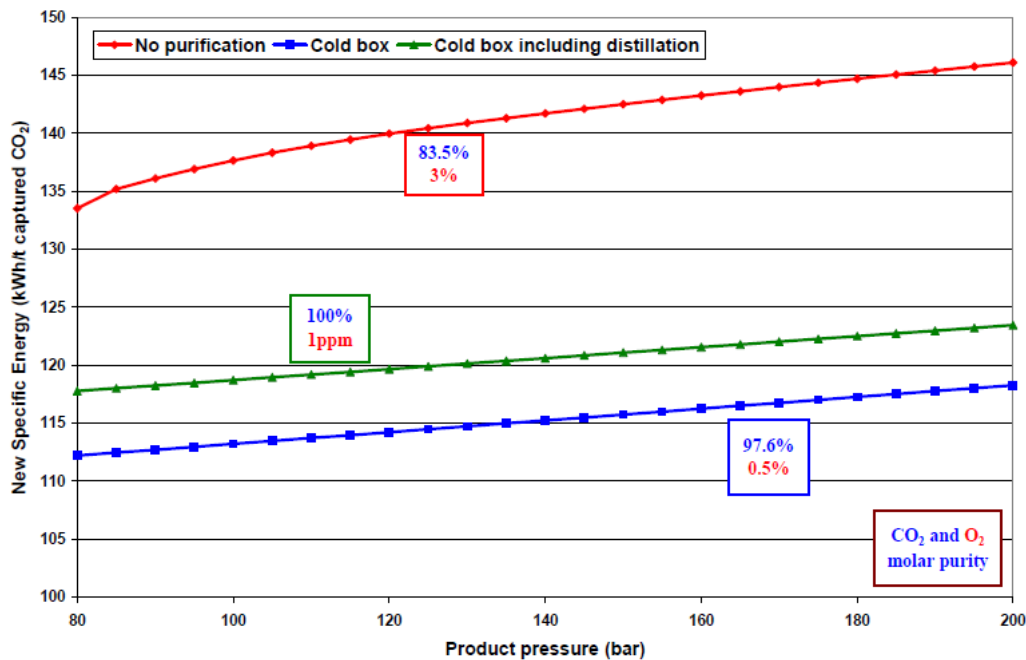


Figure 3.8: Specific energy consumption as a function of product pressure for 83 % inlet CO₂ (dry basis) and no integration. (Darde et al., 2009)

3.4.3 Requirements for CO₂ Purity and Transportation

Requirements on the CO₂ quality are defined by requirements from CO₂ transport, storage, environmental regulations and costs. Generally, there are no high technical barriers to provide high purity of the captured CO₂. However, high purity requirements are likely to cause additional costs and energy requirements resulting in a loss of power plant output and efficiency. The key issue is to economically reduce the concentration of other compounds than CO₂ in the captured stream to acceptable levels for transport and storage and to meet given environmental and legal requirements. (Bolland, 2012)

Depending on the method of CO₂ capture used, the extent of which the CO₂ is diluted with other gases differs. In particular, the oxy-combustion method results in a number of substances with the captured CO₂. Table 3.1 gives a typical composition from oxy-combustion.

Table 3.2: Typical composition of streams for the oxy-combustion technology (Adapted from Bolland, 2012)

Component	Amount
CO ₂	> 90 vol-%
CO	trace
H ₂ O	N/A
H ₂ S	trace
SO _x	< 2.5 vol-%
O ₂	< 3 vol-%
N ₂	0.6-7 vol-%
Ar	< 5 vol-%
H ₂	trace
NO _x	<0.25 vol-%

At present, no standards for CO₂ purity exist. However, quite some work has been carried out to determine proper specifications. Examples for operational conditions and recommendations found and proposed by studies are given in Table 3.3.

The first column shows exhaust gas composition for the US Canyon Reef project, where captured CO₂ from some Shell Oil Company processing plants is moved to the Val Verde basin (IPCC-CCS, 2005).

The second column shows requirements for composition for the Weyburn-Midale pipeline and EOR (IPCC-CCS 2005); here CO₂ is transported about 330 km from the Great Plains Synfuels Plant in the USA to the Weyburn-Midale EOR project in Saskatchewan, Canada. The rather high fractions of H₂S should be noted. One could say that this project is not only capturing and storing CO₂, but also the sulfur is dealt with in the same way. There is a comprehensive experience in Western Canada for sour gas (H₂S and CO₂) injection in the ground, where the sour gas captured is from produced natural gas. The Weyburn-Midale pipeline is going in a sparsely populated area, where a pipeline rupture would have less impact to humans. If such a pipeline goes through a densely populated area, it is highly questionable whether so much H₂S would be allowed.

The numbers in the third column comes from Kaarstad and Hustad (2003), showing composition for purified flue gas coming from the CO₂ capture demonstration plant at the Esbjergværket power plant in Denmark. The CO₂ gas has been planned to be transported to the Gullfaks field in the North Sea and used for EOR.

Finally, the fourth column shows Kinder Morgan's specifications for CO₂ pipeline transport and use in EOR (de Visser, Hendriks et al. 2008). The last three lines (NETL, Dynamis and Ecofys) are recommendations made by the respective project or organisation. (Bolland, 2012)

Table 3.3: CO₂ quality requirements for transport and storage (Adapted from Bolland, 2012)

Component	Canyon Reef EOR	Weyburn EOR	Esbjerg EOR	Kinder Morgan EOR	NETL	Ecofys	Dynamis
CO ₂	> 95 %	96 %	99.5%	> 95 %	-	> 95 %	> 95 %
CO	-	0.10 %	<10 ppmv	-	-	-	2000 ppm
H ₂ O	No free water, <0.489 m-3 in the vapour phase	<20 ppmv	Steam content equivalent to saturation at 5°C	<257 ppm corrosion (specified as 30 lbs/(Mmsetf)	Steam content equivalent to saturation at dew point 233K	<500 ppm (lower level recommended)	500 ppm (technical limit)
H ₂ S	<1500 ppm (weight)	0.9%	-	-	-	not critical	200 ppm
SO ₂	-	-	<10 ppmv	-	-	not critical	100 ppm
Total sulfur	<1450 ppm (weight)	-	-	-	-	-	-
N ₂	4 %	<300 ppmv	<0.48 %	< 4 %	<300 ppmv	<4 %	<4 % (including H ₂ & Ar)
NO _x	-	-	<50 ppmv	-	-	not critical	100 ppm
O ₂	<10 ppm (weight)	<50 ppmv	<10 ppmv	<10 ppmv	<40 ppmv	<4 % (total non condensable)	<4 % (Aquifier) <100 ppm (EOR)
Glycol	4x10 ⁻⁵ l/m ³	-	-	4x10 ⁻⁴ l/m ³	-	-	-
CH ₄	-	0.7 %	-	-	-	<4 %	<4 % (Aquifier) <2 % (EOR)
C ₂ +	-	2.3 %	-	-	-	-	-
Hydrocarbon	<5 %	-	100 ppmv	<5 %	-	-	-
Temperature (°C)	<120 F (≈ 48.9°C)	-	-	<50 °C	-	<30 °C	-
Pressure (Mpa)	-	15.2	-	-	15.2	-	-

As seen from Table 3.3 it is a general consensus in the scientific community that the CO₂ concentration should be higher than 95 %. There is at present no common standard for allowed level of impurities in the CO₂ going to storage. The requirement for the H₂O content in the transportation ready CO₂ is normally very stringent because of corrosion in the presence of free water, which necessitates going below the fraction given by phase equilibrium. Another technical reason is the formation of carbonic acid of hydrates, which can lead to corrosion and plugging respectively.

In case of storage of CO₂ in aquifers, the limits will be less stringent except for the limitations that are found in the handling and transportation system before storing the CO₂.

Generally, the transport of CO₂ in pipelines can only be carried out in an efficient way if the pressure is kept over the critical point value (>80 bar) and hence the fluid is in the so-called dense phase. This kind of state is accompanied by the following characteristics and benefits:

- low viscosity
- relatively high density and sensitivity to temperature changes
- compressibility factor shows non-linear behaviour
- ability to act as solvent

3.5 CO₂ capture efficiency calculations

3.5.1 Theory of separation

An important parameter in CO₂ capture and storage is the exergy lost by mixing, which represents the theoretical minimum work requirement for separation, W_{rev} [kJ]:

$$W_{rev} = -T_0 R_u \sum_i n_i \ln y_i \quad (3.6)$$

where T_0 is separation temperature [K], R_u is the universal gas constant [kJ/kgK], n_i is the number of moles of component i and y_i is the mole fraction of component i .

Written per unit mole of the ingoing gas mixture, \bar{w}_{rev} [kJ/kmol] is:

$$\bar{w}_{rev} = -T_0 R_u \sum_i y_i \ln y_i \quad (3.7)$$

Given that there are more than two gas components present in a mixture to be separated, two distinctions need to be made:

- 1) Full separation: All the i gas components are separated from each other
- 2) Partial separation: One gas component is separated from the $N-1$ other gases

The difference between 1) and 2) is illustrated in Figure 3.9.

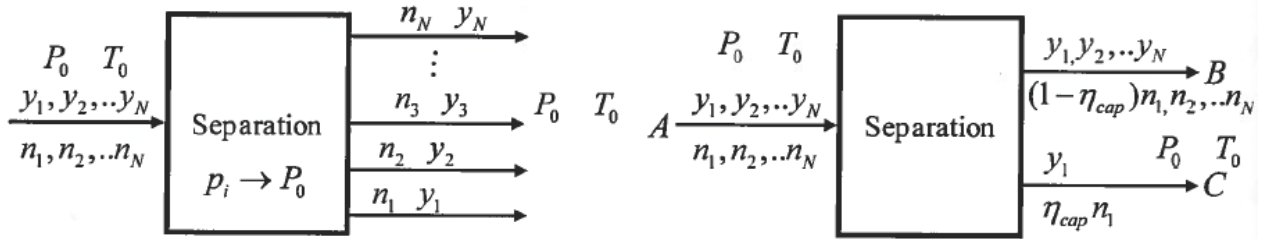


Figure 3.9: Complete separation (left) and partial separation (right) of N gas components (Bolland, 2012).

The η_{cap} includes the possibility that the separation of component 1 is not complete, which is usually the case for CO₂ separation.

For CO₂ capture, 2) is of main importance. The minimum work of separation is obtained by calculating the minimum work of separation for the incoming stream (A) and subtracting that of the outgoing streams (B and C), see Equation 3.8.

$$\begin{aligned} \bar{w}_{rev} &= \bar{w}_{rev,A} - \bar{w}_{rev,B} - \bar{w}_{rev,C} \\ &= -T_0 R_u \sum_N n_{i,A} \ln y_{i,A} + T_0 R_u \sum_{i=1}^N n_{i,B} \ln y_{i,B} + T_0 R_u n_{i,C} \ln y_{i,C} \end{aligned} \quad (3.8)$$

3.5.2 Relating work requirement for CO₂ capture and efficiency

The power plant efficiency (η) based on the lower heating value (LHV) of the fuel is commonly defined as in Equation (3.9) (Bolland, 2012):

$$\eta = \frac{W}{Q} \left[\frac{kWh_{work}}{kWh_{fuel\ LHV}}, \frac{MJ_{work}}{MJ_{fuel\ LHV}} \right] \quad (3.9)$$

In order to relate the minimum work requirement for separation to the efficiency penalty it is necessary to quantify how much CO₂ is generated in combustion of a given fuel. A CO₂ emission index (χ) is defined in Eq. X as the mass of CO₂ generated per lower heating value of the fuel.

$$\chi = \frac{m_{CO_2}}{Q} = \frac{m_{CO_2} \eta}{W} \left[\frac{kg\ CO_2}{MJ_{fuel\ LHV}} \right] \quad (3.10)$$

The reduction in efficiency caused by the minimum work requirement can then be expressed as:

$$\Delta\eta = \frac{w_{rev,CO_2} m_{CO_2}}{Q} = w_{rev,CO_2} \chi \left[\frac{MJ_{work}}{MJ_{fuel\ LHV}} \right] \quad (3.11)$$

In addition, the CO₂ emissions per kg of clinker produced is a widely used parameter in the cement industry.

$$C_{CO_2} = C_e \chi \left[\frac{kg\ CO_2}{kg\ clinker} \right] \quad (3.12)$$

Where C_e is the specific energy use of the cement making process in terms of heat consumption per ton of produced clinker, given by Eq. (3.12):

$$C_e = \frac{Q_{fuel}}{m_{clinker}} \left[\frac{MJ_{fuel\ LHV}}{kg\ clinker} \right] \quad (3.13)$$

3.5.3 CO₂ avoided, CO₂ captured and CO₂ capture efficiency

In CO₂ capture, it is useful to characterise how much CO₂ is captured and how much CO₂ is actually avoided when CO₂ is captured compared to no capture. Capturing CO₂ might require more fuel to be used per ton clinker produced, and the additional fuel that is used generates more CO₂, causing a difference in the terms ‘avoided’ and ‘captured’.

The CO₂ capture ratio, Φ, is defined as the fraction of CO₂ formed which is captured and subsequently stored:

$$\Phi = \frac{\dot{m}_{CO_2\ captured}}{\dot{m}_{CO_2\ formed}} \left[\frac{kg\ CO_2\ captured}{kg\ CO_2\ formed} \right] \quad (3.14)$$

In order to characterise a plant’s CO₂ capture ability, the term **CO₂ captured** can be used. This is defined as the amount of CO₂ captured per tonne clinker produced.

$$CO_2\ captured = \frac{\chi}{\eta_{CO_2}} \eta_{cap} \left[\frac{kg\ CO_2}{kg\ clinker\ produced} \right] \quad (3.15)$$

It is also useful to define the amount of **CO₂ emitted**, which is the amount of CO₂ emitted per main product per tonne clinker produced.

$$\text{CO}_2 \text{ emitted} = \frac{\chi}{\eta_{\text{CO}_2}} (1 - \eta_{\text{cap}}) \left[\frac{\text{kg CO}_2}{\text{kg clinker produced}} \right] \quad (3.16)$$

The term **CO₂ avoided** is the additional CO₂ generated because of the applied CCS technology, and is defined as the net reduction of CO₂ emissions per unit of net power output comparing a reference plant without CO₂ capture and that of a similar power plant with CO₂ capture.

$$\text{CO}_2 \text{ avoided} = \frac{\chi}{\eta_{\text{ref}}} - \frac{\chi}{\eta_{\text{CO}_2}} (1 - \eta_{\text{cap}}) \left[\frac{\text{kg CO}_2}{\text{kg clinker produced}} \right] \quad (3.17)$$

The **CO₂ capture efficiency** is defined as the ratio between the net reduction of CO₂ emitted per unit clinker produced comparing to a reference plant without CO₂ capture and that of a similar plant, and the emission of CO₂ per unit clinker produced of the reference plant. This equals to the ratio between CO₂ avoided and the emissions of CO₂ per unit of clinker produced of the reference plant. If there is no efficiency penalty associated with CO₂ capture, the CO₂ capture efficiency will be equal to the CO₂ capture ratio.

The oxy-combustion method has a capture ratio close to 100 %, because no additional fuel is used in this technology when applied to cement production. Consequently, there is no significant difference between CO₂ capture efficiency and CO₂ capture ratio for oxy-combustion in a cement plant. The term CO₂ capture ratio is therefore chosen as the term used to quantify the CO₂ capture efficiency in this thesis.

3.6 Limits and Barriers for CCS in the Cement Industry

CCS is certainly a technology which – due to the expected cost - will have a strong impact on any industry in which it is applied. Today, the costs for carbon capture are expected to be still very high and in the range between 40 and 100 € per t of CO₂, not taking into account additional costs for CO₂ transport and storage. (ECRA, 2012)

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

Regulatory frameworks for CCS projects are still pending. Key questions concerning e.g. licensing and permitting procedures, monitoring, long-term liability and risk management of storage sites, pipeline access, etc. are still open. In the European Union, the CCS Directive is intended to provide the legal framework for CCS projects. The directive had to be implemented in the national legislation of the individual member states by 25 June 2011. However, at the end of 2011 only two Member States (Spain and Romania) had met their obligation, despite the deadline of 25 June 2011. The European Commission has started formal infringement proceedings against those Member States who have yet to implement the directive in their national laws. (Global CCS Institute, 2012) This underlines the basic lack of public acceptance for CO₂ storage.

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

Due to the limited CO₂ pipeline infrastructure, there are only few specifications regarding the purity of the compressed CO₂ gas stream, see Table 3.3. However, the separation of impurities in the CO₂ would significantly affect the costs of CO₂ capture technologies. A report about this was published by the IEA GHG with support from the Global CCS Institute (GCCSI). (IEA GHG, 2011)

Finally it is not clear how CO₂ storage can be managed not only in large scale application but even for demonstration projects. According to the existing CCS roadmaps, the so-called BLUE Map scenario would require 1.2 Gt of CO₂ storage capacity in 2020 and 145 Gt of worldwide CO₂ storage capacity in 2050. In principal, captured CO₂ can be stored in different types of underground storages, like saline aquifers, depleted oil or gas fields or coal seams. Enhanced Oil Recovery (EOR), which involves CO₂ injection and storage, has been used by the oil and gas industry for more than 40 years. Long-term experience in CO₂ injection is available e.g. from the

Sleipner project (~ 1 Mt CO₂/yr injected to the Utsira reservoir) and the Snøvit LNG project (~ 0.75 Mt CO₂/yr) in Norway, the Weyburn project (2.7 – 3.2 Mt CO₂/yr) in Canada and the In-Salah project in Algeria (~ 1.2 Mt CO₂/yr). (ECRA, 2012 and Bolland, 2012)

In Europe, two major research projects (GESTCO and GeoCapacity) have been carried out to identify and characterise potential CO₂ storage sites and to assess the European capacities for the storage of CO₂. Based on this an atlas of European CO₂ storage sites has been developed. For central and northern Europe, the North Sea could offer significant storage capacities, but up to now there is no concept for appropriate CCS infrastructure.

With respect to public awareness and acceptance of CO₂ capture and storage a survey which was carried out in several European countries showed that only a small percentage (10 %) of the European population is aware of the concept of carbon capture and storage for climate protection (ECRA, 2012). In this context, the storage of CO₂ is highly controversial in the public discussion. As a result of this, the exploration of storage sites, which has been started in connection with planned demonstration projects, was stopped in several cases due to public resistance.

3.7 Technical Issues of Oxy-combustion in a Cement Plant

Some of the major technical issues related to oxy-combustion cement production are [Barker et al., 2009]:

- **Flame Temperature and Dilution.** Flame temperatures in excess of 3500 °C can be achieved in oxygen combustion. This is too hot for normal operation and it is therefore essential that a proportion of the CO₂-rich flue gases are recycled back to the combustion zone to provide the necessary dilution.
- **Heat Transfer Characteristics.** The radiant heat fluxes and convective heat transfer performance of the combustion chamber are a function of the gas composition in the chamber. Changing the atmosphere within the combustion chamber will have a significant effect on the heat transfer characteristics.
- **Feed Lifting.** It has been reported that nitrogen ballast in the exhaust gases from the kiln plays an important role in lifting the feed between the cyclone stages in the suspension preheater of a modern cement kiln. CO₂ is a denser gas than nitrogen and should be more effective in this feed lifting role within the suspension preheater.
- **Wear and tear.** Due to the higher temperatures it is generally understood that cement kiln wall deterioration will increase at higher oxygen concentrations. Hence, there is a balance between achieving the high temperatures for the cement production process and having to replace the kiln wall lining.
- **Process chemistry.** Research is on-going to determine whether the clinker formation in a different atmosphere will still generate a useful product. Testing performed by ECRA (2012) showed only slight variances (below 3 %) in properties like strength development and compressive strength compared to standard cements. According to this, negative impact of oxy-combustion on the product quality seems to be negligible.
- **Air Dilution.** Significant air in-leaks occur in the raw mill, preheater and kiln. Excessive air in-leaks will result in contamination of the CO₂-rich exhaust gas. These contaminants will require removal and will increase the costs of operating an oxy-combustion process. Any design for an oxy-combustion cement process should minimise air in-leaks.
- **Flue gas Clean-up.** Depending on the final storage location of the CO₂ the gas will require some clean-up to remove water vapour, nitrogen, argon, NO_x or SO_x.
- **Air Separation Unit (ASU).** An ASU will be required to deliver oxygen to the oxy-combustion process. This will increase the electricity demand of the plant compared with a conventional cement plant. The power required by a cryogenic oxygen plant is typically in the range 200-240 kWh/tO₂.

4 Process Simulation Model and Methodology

4.1 Simulation software

The simulation software used in this thesis is Aspen HYSYS version 8.3. Aspen HYSYS is a comprehensive process modelling software, widely used in the oil and gas industry and by engineering companies to optimize process design and operations. Both steady-state and dynamic simulation models can be created in HYSYS. For the purpose of this thesis, only steady-state simulations have been employed. The simulation models are based on process flow diagrams acquired through the literature study and further developed from de Winter's project thesis (2013).

4.2 Fluid Property Packages in Aspen HYSYS

The property packages available in HYSYS allow for the prediction of properties of mixtures ranging from well-defined light hydrocarbon systems to complex oil mixtures and highly non-ideal (non-electrolyte) chemical systems. HYSYS provides enhanced equations of state (EOS) for rigorous treatment of hydrocarbon systems (Peng-Robinson (PR) and improved Peng-Robinson (PRSV)); semi empirical and vapour pressure models for heavier hydrocarbon systems; steam correlations for accurate steam property predictions, and activity coefficient models for chemical systems. Each of these equations has their own limitations. (AspenTech, 2003)

Selection of an appropriate property package is a key requirement of process design, in order to accurately reproduce the various physical properties for the system in question. Table 4.1 lists some typical systems and recommended correlations.

Table 4.1: Recommended Property Methods (Adapted from AspenTech, 2003)

Type of System	Recommended Property Method
TEG Dehydration	PR
Sour Water	PR, Sour PR
Cryogenic Gas Processing	PR, PRSV
Air Separation	PR, PRSV
Reservoir Systems	PR, PR Options
Steam Systems	Steam Package, CS or GS
Hydrate inhibition	PR
Chemical systems	Activity Models, PRSV

The Peng-Robinson EOS is generally the recommended property package for oil, gas and petrochemical applications. It rigorously solves any single, two-phase or three-phase system with a high degree of efficiency and reliability, and is applicable over a wide range of conditions, as shown in Table 4.2, where it is compared to Soave-Redlich Kwong (SRK).

Table 4.2: Application ranges for PR and SRK (Adapted from AspenTech, 2003)

Method	Temp (°C)	Pressure (kPa)
PR	> - 271	< 100,000
SRK	> -143	< 35,000

The Peng-Robinson equation of state supports the widest range of operating conditions and the greatest variety of systems. The PR, PRSV and SRK equations of state generate all require equilibrium and thermodynamic properties directly.

The recommended property methods for Cryogenic Gas Processing and Air Separation are the Peng-Robinson EOS (PR) or the Peng-Robinson-Stryjek-Vera EOS (PRSV). The PRSV can handle the same systems as the PR equation with equivalent or better accuracy, plus it is more suitable for handling moderately non-ideal systems. The only compromise is increased computational time and the additional interaction parameter that is required for the equation.

The chosen property package for the simulations performed in this thesis is the PRSV, as this is the most accurate property method for the simulated processes. PRSV was also the property method chosen in the project thesis by de Winter (2013), and using the same equation of state makes direct comparison of simulation results easier, as effects of EOS differences need not to be adjusted for.

4.3 Existing Oxy-combustion Cement Process Configurations

In the Technical Study published by IEA in 2009, four possible configurations for an oxy-combustion cement plant were developed. The configurations are illustrated in Figure 4.1 to Figure 4.3, and can be summarised as:

- **Configuration 1:** Diversion of preheater exit gases for fuel drying and subsequent capture and recycle
- **Configuration 2:** Capture and recycle of all flue gases from cement plant with diversion of cooler exhaust for fuel drying
- **Configuration 3:** Capture and recycle of all flue gases from cement plant with diversion of cooler exhaust for fuel drying and a ‘leak-free’ raw mill
- **Configuration 4:** Dual preheaters with oxy-combustion in the precalciner only.

In all cases the clinker cooler is excluded from the oxy-combustion operation and thus is operated with ambient air.

In addition, a process configuration was developed by ECRA (2009), and is described in Chapter 4.3.5. The HYSYS model constructed by de Winter (2013) is also described.

4.3.1 IEA GHG Configuration 1

In the first configuration (Figure 4.1) both kiln and pre-calciner firing are supplied with oxygen (95 % O₂, 2 % N₂, 3 % Ar) from an air separation unit. This makes it essential to reduce air in-leaks in these plant components. In this layout, both the CO₂ generated in the preheater and in the kiln is captured. 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. In 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 requirements 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.

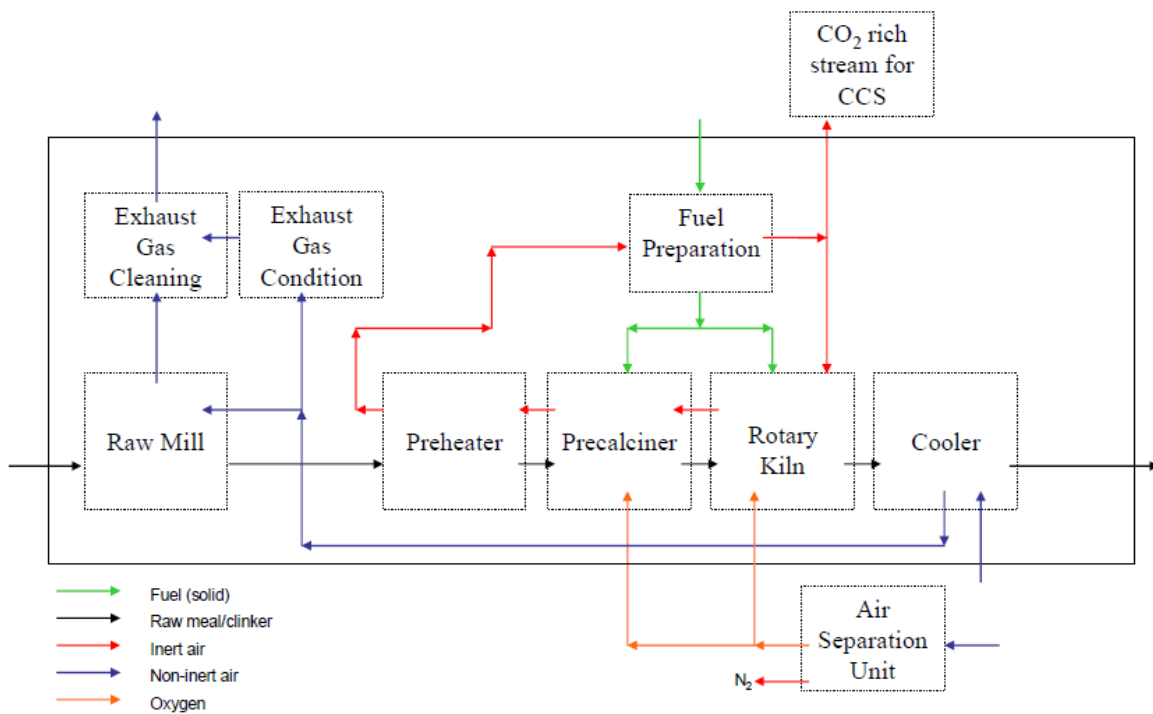


Figure 4.1: Oxy-combustion Cement Plant Configuration 1 – Diversion of preheater exit gases for fuel drying and subsequent capture and recycle (IEA, 2008).

4.3.2 IEA GHG Configuration 2

The second configuration (Figure 4.2) is quite similar to the first configuration. 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.

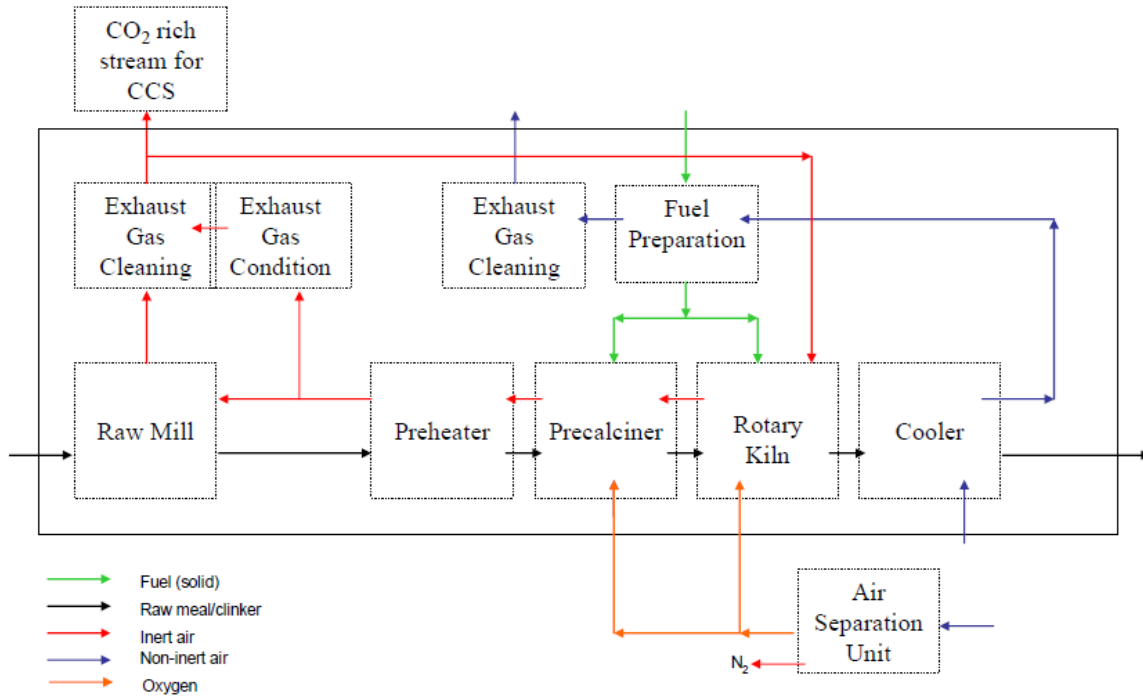


Figure 4.2: Oxy-combustion Cement Plant Configuration 2 – Capture and recycle of all flue gases from cement plant with diversion of cooler exhaust for fuel drying (IEA GHG, 2008).

4.3.3 IEA GHG Configuration 3

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 consequently increased costs.

4.3.4 IEA GHG Configuration 4

The fourth and last configuration proposed by IEA (Figure 4.3) shows a dual preheater system with oxy-combustion in the pre-calciner only. This configuration has been chosen by the authors as the most promising one though only about 60 % of the CO₂ produced are captured. The flue gas from the pre-calciner is led into the preheater string 2, from which the gas is transmitted to the CO₂ compression facility and partially recirculated to the pre-calciner. The recycled stream is heated up to temperatures approaching the pre-calciner 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 approximately 250 °C. Before the CO₂ purification unit, the gas stream is dedusted by an electrostatic precipitator (ESP). It was assumed that an ESP operates better at those high temperatures than a bag filter. The oxy-combustion 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 are necessary.

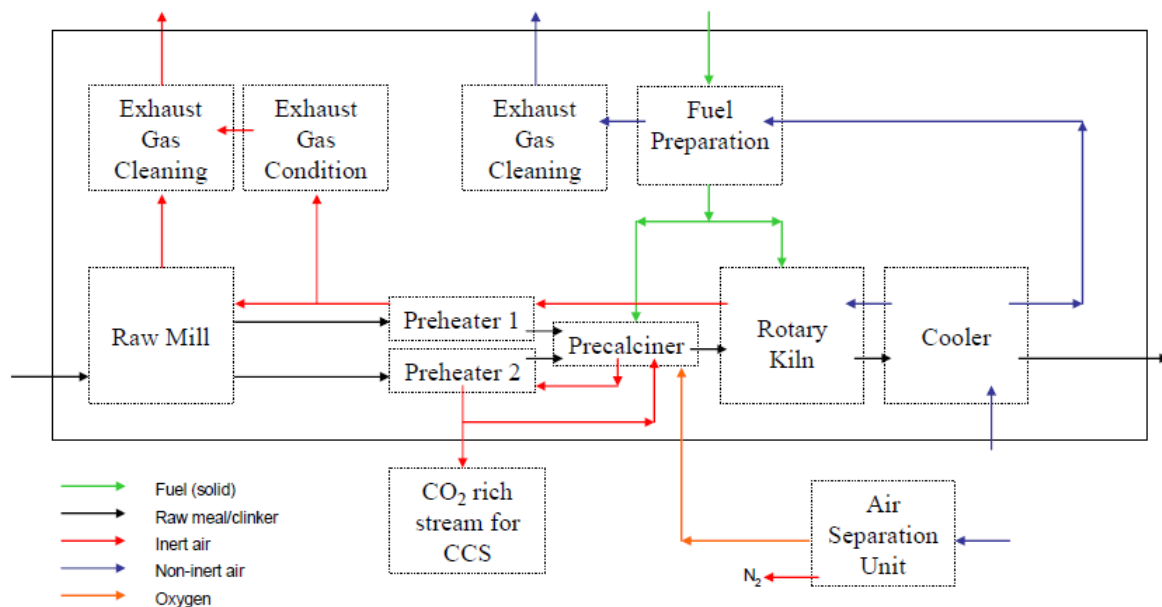


Figure 4.3: Oxy-combustion Cement Plant Configuration 4 - Dual preheaters with oxy-combustion in the pre-calciner only (IEA, 2008).

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 oxy-combustion 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.

4.3.5 ECRA Oxy-combustion Configuration

In addition to the four configurations proposed by IEA GHG (2008), an oxy-combustion configuration was developed by ECRA in the Technical Report from 2009. The principal configuration of an oxy-combustion cement plant, of which the modelling of the clinker burning process is based, remains nearly unchanged to the conventional technology and is illustrated in Figure 4.4.

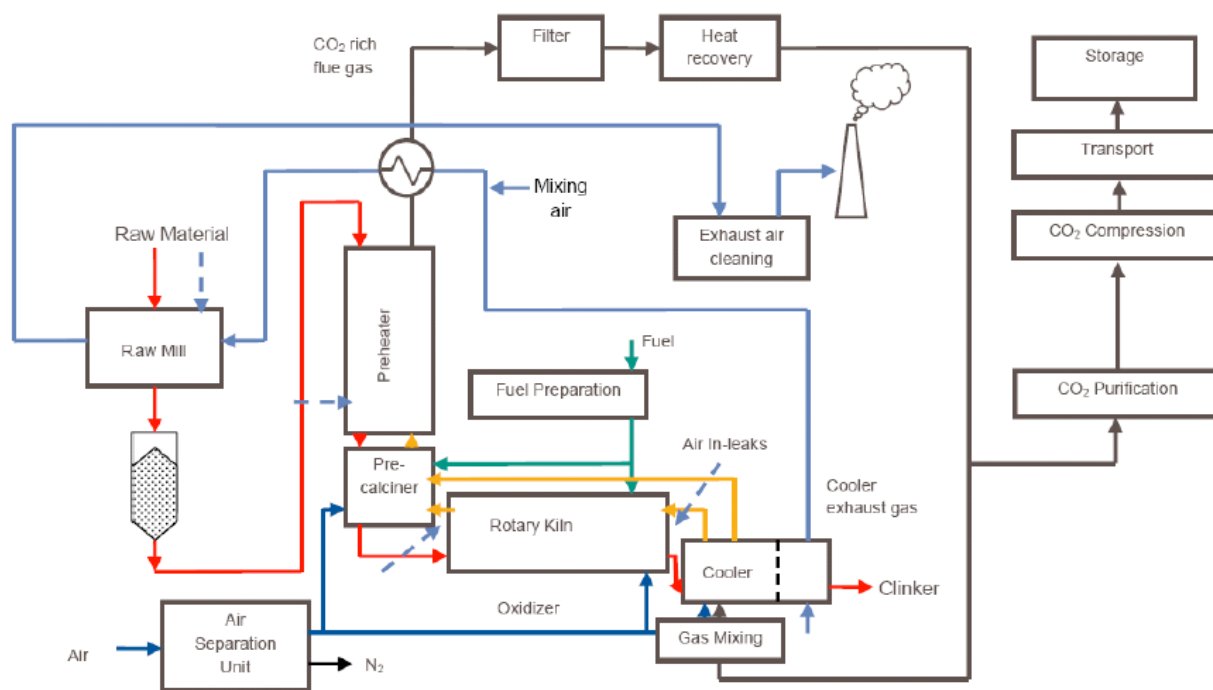


Figure 4.4: Oxy-combustion Plant Configuration 5 (ECRA, 2009).

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 added. 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 is an issue in oxy-combustion 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 economic problems. To avoid the necessity of an air tight raw mill the cooler exhaust gas, which consist of ambient air, is used for drying.

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, and must be supplied by an on-site oxygen supply system. The oxidizer composition in ECRA’s model is assumed to be: 95 % oxygen, 1.5 % nitrogen and 3.5 % argon.

A summary of the specifications is listed in Table 4.3. In addition a comparison including the disadvantages (orange) and advantages (green) of the described solutions of the ECRA Configuration and the IEA GHG Configuration number 4 is given.

Table 4.3: Comparison of the configurations for retrofitting and new built plants (ECRA, 2009)
Note: Figure 4-13 and Figure 4-14 equals Figure 4.3 and Figure 4.4 in this thesis.

	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

4.3.6 Jelmer de Winter's Oxy-combustion Layout

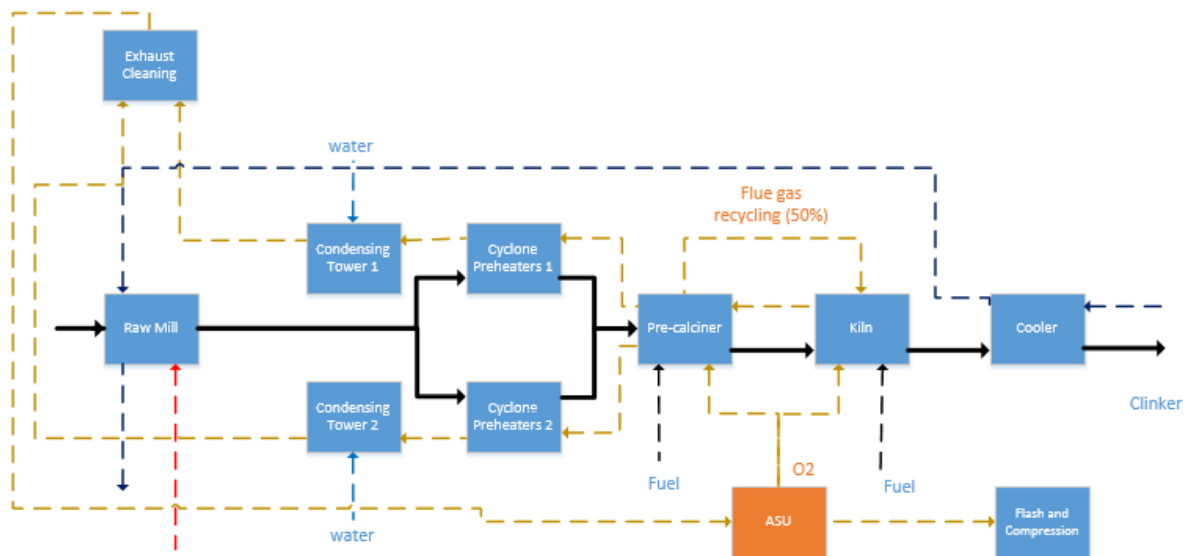


Figure 4.5: Jelmer de Winter's Oxy-combustion Layout.

Figure 4.5 shows the simulation model constructed by de Winter (2013). It is modelled using Apen HYSYS and based on the IEA Configuration number 4 and according to data provided by Norcem.

The raw mill is decoupled from the rest of the process, and oxygen from the ASU is preheated by the flue gas, based on the heat integration guidelines given by IEA GHG (2008). The combustion gas from the pre-calciner is recycled back to the kiln at a 50 vol-% recycle rate. The CO₂ concentration in the flue gas stream is 74 %.

4.4 Chosen Oxy-Combustion Cement Plant Model in this Thesis

The simulation layout chosen in this thesis is further developed from the oxy-combustion model by de Winter (2013) and the process model suggested by ECRA (2009). The simulation model is designed as a stationary simulation file in HYSYS. Figure 4.6 shows a process flow diagram of the HYSYS model made during this thesis work. A more detailed description can be found in Appendix A and Appendix B. The main improvement steps are as follows:

- The ECRA oxy-combustion layout was chosen over the IEA GHG layout, as ECRA's layout captures the CO₂ from both the pre-calciner and the kiln, giving a CO₂ capture rate of above 90 %. The IEA GHG Configuration 4, which de Winter (2013) based his HYSYS model on, only captures around 60 % of the CO₂ emissions.
- Energy consumption of the ASU with 95 % oxygen purity is reduced from 0.229 kWh/kg O₂ to 0.198 kWh/kg O₂, after discussions with post.doc. Chao Fu.
- A two-staged clinker cooler replaces the air-cooled clinker cooler used by de Winter (2013), after recommendations from ECRA (2012). As a result, no pre-heating of the recycled flue gas is necessary.
- The CO₂ CPU is improved to give a product CO₂ purity of >95 %.

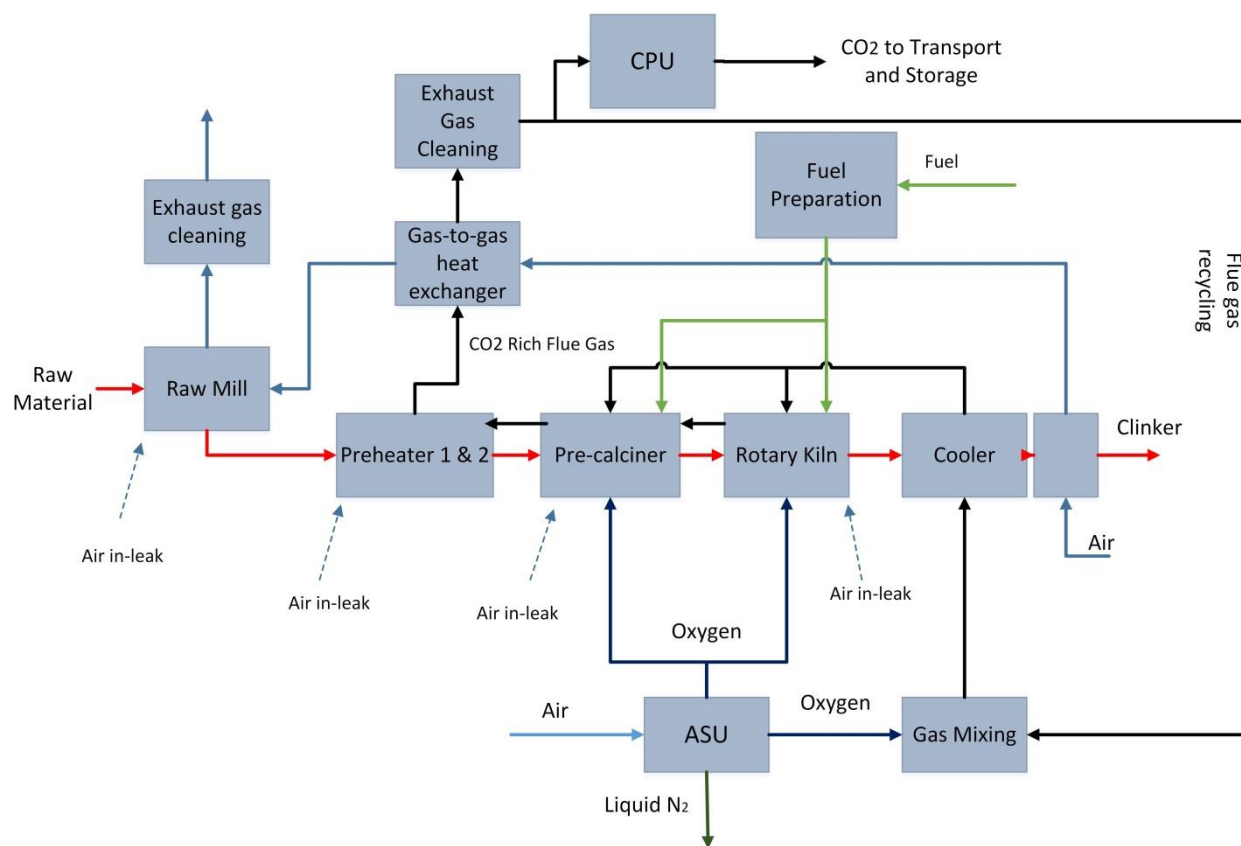


Figure 4.6: Oxy-combustion cement plant layout as modelled in this thesis.

4.4.1 Overall Assumptions

The main technical assumptions used for this study are based on the IEA GHG 2008 Technical Report, the ECRA Technical Reports from 2009 and 2012 and information from Bolland (2012).

The key points are summarized below:

Site conditions

- Ambient air temperature: 15 °C
- Ambient air pressure: 1.013 bar

Pre-calciner

- It is assumed that the pre-calciner is fed with Refuse Derived Fuels (RDF) only, as assumed by de Winter (2013).

Kiln

- It is assumed that the kiln is fed with coal only. This was also assumed by de Winter (2013).

ASU and O₂ Purity

- The O₂ purity supplied by the air separation unit (ASU) was specified at 95 mol %. This is derived from several previous studies (IEA, 2008 and ECRA, 2009).
- N₂ content in O₂ supplied by the ASU: 2 mol%
- Argon content in O₂ supplied by the ASU: 3 mol%

CO₂ Processing

- For consistency with other studies, the minimum CO₂ capture rate is chosen to be 80 %, with a preferred level of around 90 %.
- CO₂ is to be compressed to 110 bara before injection into the transfer pipeline.

Seawater

- It is assumed that sea water is available for cooling.
- Average seawater temperature: 12 °C
- The pinch point difference in the seawater coolers is assumed to be >10 K, meaning that the flue gas can be cooled down to a minimum of 20 °C.

Heat and pressure loss

- No heat loss in any components
- No pressure loss in piping system

Efficiencies of compressors and pumps

- Adiabatic efficiency of compressors is set to 80 %
- Polytrophic efficiency of pumps is set to 75 %

Pressure drop

- Pressure drop in heat exchangers is set to 30 kPa, equal to ~3 % of inlet pressure (1 atm)

Air in-leakage

- Air in-leakage in the proposed solution is assumed to be 2 % of total gas flow
- To simplify, one total air in-leak is modelled, instead of separate air in-leaks at the different in-leakage points.

4.4.2 Cement Model specifications

The cement process is modelled as a block flow diagram, where most of the energy intensive processes are represented as black boxes receiving heat from the flue gas stream. The heat and mass balances over these blocks were calculated to know the maximum enthalpy drop of the CO₂ rich flue gas at different stages in the process. The cement process modelling is based on the HYSYS model created by de Winter during his project work, and is modelled according to data provided by Norcem and case study data from the IEA GHG (2008) and ECRA (2009). Due to limitations in HYSYS when it comes to modelling of solid components, only the flue gas streams are modelled, not the clinker making process. The NO_x, NO₂ and SO₂ streams are neither modelled, as the modelling of the NO_x and SO_x removal units is not a part of the scope of this thesis.

The known values are flow rates and temperatures of the total flue gas streams at different points in the cement process. No heat duties are known for the kiln, pre-calciner, preheaters, cooler and the raw mill in this specific cement plant, so the heat duties transferred from the flue gas to the raw material are obtained by using the temperature difference over the process block and flue gas specific heat. Figure 4.7 shows the model of the cooler, kiln and pre-calciner.

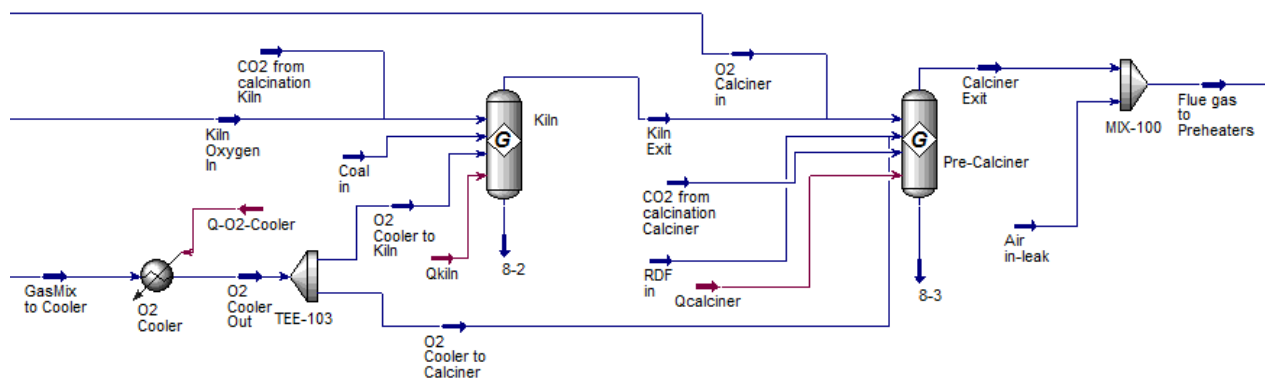


Figure 4.7: Kiln and Calciner in HYSYS.

The raw material is assumed to be a function of the heat transferred by the flue gas within the kiln and pre-calciner and the heating value of the primary fuel. To be able to calculate these heat duties, a Gibbs reactor is modelled using fixed inlet and outlet streams. The Gibbs reactors are designed to calculate the equilibrium composition of the product stream by minimising its Gibbs free energy, constrained by conservation of atomic species using the composition of the feed stream.

The Gibbs free energy, originally described as “available energy” by J. W. Gibbs in 1873, is a thermodynamic potential that measures the “usefulness” or process-initiating work obtainable from a thermodynamic system at a constant temperature and pressure.

CO₂ emissions are calculated based on mass balances over both Gibbs reactors. Since the fuel flow, the inlet stream to the kiln and outlet stream of the pre-calciner are known, both reactors are modelled as one black box, assuming all calcination occurring in the pre-calciner, according to Equation (4.1).

$$\sum_i (C_{in,i} + O_{2,in,i}) = \sum_i (CO_{2,out} - CO_{2,calcination}) \quad (4.1)$$

The cooler is modelled as a two-stage cooler, according to ECRA 2009, with one oxygen-stream and one air-stream.

The air in-leakages are modelled as one air in-leak, in order to more easily run sensitivity analysis. In reality, there are several air in-leakages in the plant, as indicated in Figure 4.6.

The recirculation rate is kept at 0.5, as suggested by both ECRA (2012) and IEA GHG (2008).

4.4.3 Heat Duties

Heat duties of the cooler and raw mill are calculated based on the IEA GHG report (2008), since the heat duties of the cement plant itself are unknown. Heat duties are expressed in terms of clinker production, which makes it applicable to the Brevik cement plant, assuming comparable raw material flows.

The heat duties of the kiln and pre-calciner represent the enthalpy transferred from the fuel to the raw material flow. These values are obtained by using a Gibbs reactor, with known input and output flow specifications of the flue gas. Mass flow, composition and temperature levels of the flue gas are known. The difference in inlet and outlet enthalpy is expressed as negative heat duties within the Gibbs reactors.

4.4.4 CO₂ from Calcination

The raw material mass flow of limestone (CaCO₃) is known to be 92 kg/s on average. (Tokheim, 2011) Assuming pure limestone (M = 100.09 kg/kmol), the molar flow of the raw material will be 0.919 kmol/s. The calcination reaction of CaCO₃ into CaO and CO₂ has molar ratios of one, shown in Equation (4.2). Thus, the number of moles of CO₂ generated from the calcination process should be equal to the number of moles of limestone.



Since the flue gas stream contains other carbon rich sources emitting CO₂, the oxidation of coal and RDF is used in this study, as a more practical approach. The outlet conditions of the pre-calciner at the Norcem plant is known by measurements of the flue gas stream after the preheaters, and back calculations are performed to find pre-calciner exit specifications. A mass balance of all incoming carbon rich sources into the combustion zones (kiln and pre-calciner) and the pre-calciner exit specifications gives the CO₂ flow rate from the calcination process.

4.4.5 Fuel Specifications and Characteristics

Fuel into the kiln and pre-calciner is characterized by a mixture of coal, different kinds of waste and biomass. Fuel is fed into both the kiln and pre-calciner by respectively 40 and 60 percent on heat basis. In total, over 131 MW of heat is supplied to the cement process, resulting in a specific energy use of 3.76 MJ/kg clinker. (de Winter, 2013)

In the studied process model, the fuel into the kiln is assumed to be coal with a heating value of 23.2 MJ/kg, which is the average heating value of the fuel composition including the share of alternative fuel in the kiln. The fuel is fed into the pre-calciner consists of 56 wt-% of RDF (10.88 MJ/kg) with a biomass fraction of 60 wt-%, which results in an average heating value into the kiln of 16.0 MJ/kg. The composition of RDF will vary according to the origin of the waste,

but is assumed to have an average composition based on the CEN/TC 343 standards for 60 wt.-% biomass. The dry, ash-free composition of the coal and the composition of the RDF used for modelling purposes are shown in Table 4.4.

Table 4.4: Coal and RDF Analysis (deWinter, 2013)

Composition (wt-%)	Coal	RDF
Carbon	82.5	55.26
Hydrogen	5.6	7.21
Oxygen	9.0	35.53
Nitrogen	1.8	1.32
Sulphur	1.1	0.25
Chlorine	0	0.43
SUM	100	100

4.5 Oxy-combustion Specifications

Recommendations by the ECRA Technical Report (2009) were used for the configuration of the oxy-combustion layout. The configuration captures the CO₂ emissions both from the kiln and the pre-calciner, compared to the IEA-GHG layout that only captures the CO₂ emissions from the pre-calciner (60 %). Based on the studies performed by ECRA (2009, 2012) and IEA-GHG (2008), 50 % of the preheater exhaust gases are recirculated back to the kiln and pre-calciner, to maintain the combustion temperatures.

4.5.1 Air Separation Unit (ASU)

The ASU is modelled as a black box, where only the resulting oxygen stream is used in the HYSYS model. The chosen oxygen purity is 95 %, and the composition of the gas from the ASU is assumed to be: 95 % Oxygen, 3 % Nitrogen, 2 % Argon. The energy consumption is taken from a technical study performed by Chao Fu (2014), and is assumed to be 0.198 kWh/kg oxygen for 95 % oxygen purity. The oxygen is fed to both the kiln and the pre-calciner.

4.5.2 Specifications of the CO₂ CPU

In this section, further gas separation after H₂O condensation to achieve required CO₂ quality is evaluated. This corresponds to optimising the CO₂ CPU design to achieve a CO₂ purity of > 95 %.

The CO₂ CPU is further developed from de Winter's project thesis. The main modifications are:

- The pressure in compressor K-2 is changed from 33 bar to 26.5 bar, to achieve a 95 % CO₂ purity. De Winter's layout only achieved a CO₂ purity of 94 mol%.

- The compressed exhaust gas (mainly nitrogen) exiting from the LNG-101 is preheated in the exhaust heater and expanded to atmospheric pressure, before the gas is released to the atmosphere.
- An extra stage in the LNG-101 heat exchanger is added, to improve the process.

The CPU is designed to have a CO₂ recovery rate of at least 90 %, and a CO₂ purity of >95 %. Figure 4.8 shows the HYSYS model of the CPU.

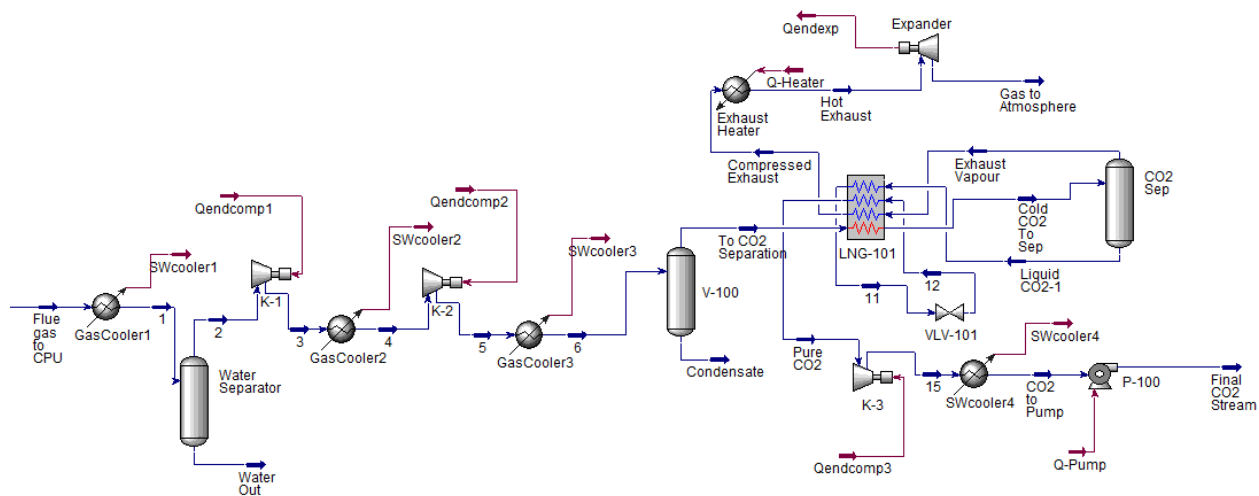


Figure 4.8: HYSYS CPU design.

After the cement plant, the water from the flue gas is separated out. The gas is then compressed in a multistage compressor with intercooling, before the gas is sent to the “cold box”, where the CO₂ is separated out. In the “cold box” the flue gas is cooled down to -54 °C at a pressure of 24 bar, forming liquid CO₂ which is separated from the rest of the flue gas in a flash tank. The liquid CO₂ exiting from the CO₂ separator (CO₂ Sep) is cooled down from -45 °C to approximately -55 °C by adding a valve and an extra side in the LNG heat exchanger.

Ideally, the CPU should be specifically designed according to the CO₂ purity specifications at the inlet, but this model is built to be able to work with a broader range of CO₂ purity in order to run a sensitivity analysis with different air in-leakages. Important parameters that needs to be adapted when the flue gas CO₂ purity changes is the pressure drop in compressor K-2 and the pressure drop in the valve VLV-101. Reducing the outlet pressure of K-2 increases the product purity, but at the same time, the CO₂ capture rate decreases.

The CO₂ stream is prepared for storage by compression and pumping up to 110 bar. Depending on the temperature, pure CO₂ will be in either liquid phase or supercritical phase (critical point at 31.1 °C and 72.05 bar), as can be seen from Figure 4.9.

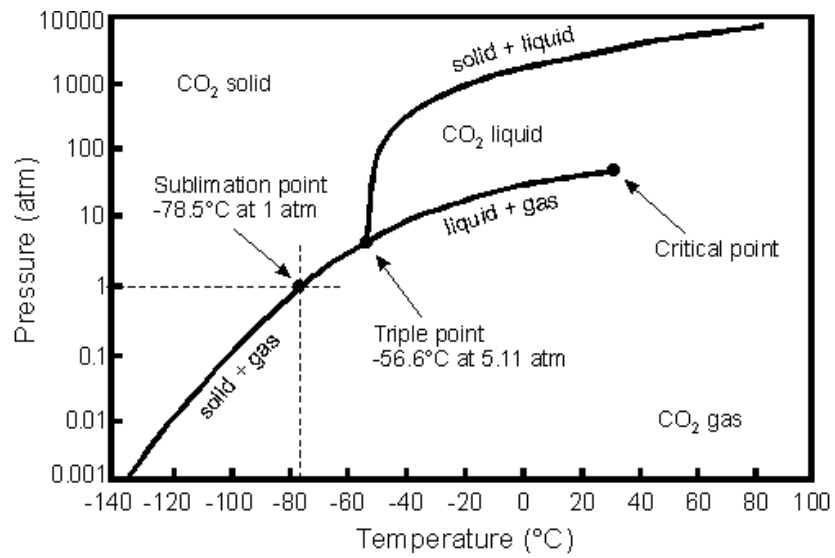


Figure 4.9: Phase Diagram of CO₂. Source: <http://stevengoddard.wordpress.com/2010/09/05/the-freezing-point-and-the-dew%20point-part-2/>.

5 Simulation Results and Discussion

5.1 General

The following chapter contains a presentation and discussion of the results obtained from the model development and process simulations. The results are compared with results from previous studies on oxy-combustion on cement plants where applicable.

5.2 Flue gas CO₂ concentration and CO₂ purity

5.2.1 Effect of air in-leakage on the flue gas composition

The model has been tested with five different air in-leakage percentages; 2, 4, 6, 8 and 10 % of total gas flow. Generally about 6 to 10 % of the flue gas from a commercial cement kiln plant consists of ambient air in-leakages, due to the slight negative operating pressure (ECRA, 2009).

Figure 5.1 shows how the air in-leakage influences the CO₂ composition in the dry flue gas (after the water separator).

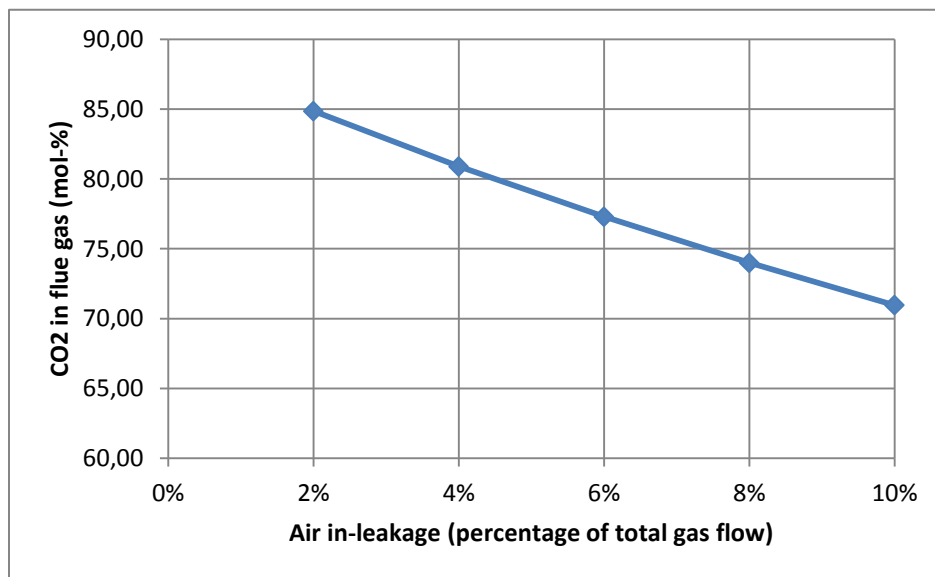


Figure 5.1: Effect of air in-leakage on the dry flue gas composition.

The figure shows that the CO₂ concentration decreases with increasing air in-leakage. The decrease in CO₂ concentration is expected, as the air in-leakage causes the flue gas to be diluted with O₂ and N₂.

5.2.2 Discussion and Comparison with previous studies

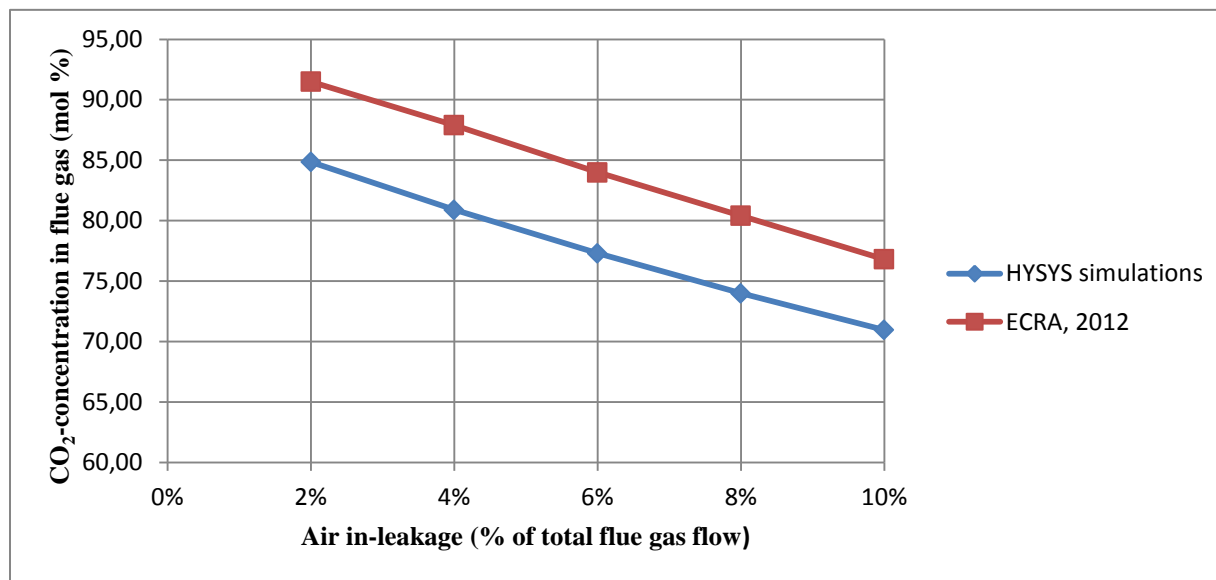


Figure 5.2: Comparison of flue gas concentration from HYSYS model with ECRA (2012).

Figure 5.2 compares the HYSYS simulation results from this thesis work with calculation results performed by ECRA in the Technical Study from 2012 (ECRA, 2012). The graphs show that ECRA achieved a higher overall flue gas CO₂ purity for all the air in-leakage rates. However, the percentage decrease in CO₂-concentration per percentage of air in-leakage is the same for both graphs. This indicates that the cement plant modelled in this thesis performs similarly to other models, although the current model can be improved in terms of achieving a higher CO₂ concentration in the flue gas.

The numbers from ECRA shows that an air in-leakage of 10 % causes a reduction in the CO₂ concentration of ~ 14.7 % compared to the case of only 2 % air in-leakage.

Simulation results from this master thesis indicate a reduction in CO₂ concentration of 14 % for the similar case.

The slopes of the curves are similar, almost linear in the investigated range, giving the same trend with increasing air in-leakage. The gradient is a 1.8 % decrease in CO₂ purity per 1 % increase in air in-leakage for the range of studies. The curves highlight the importance of preventing air in-leakages in a practical system; see also Chapter 5 for further discussions on this topic.

The difference in flue gas concentrations, found in this thesis and ECRA's simulation, is most likely a result of different flow rates in fuel and oxygen in the cement process, as well as different types of fuels used for combustion. ECRA (2009) reports that coal with a calorific value of 25 MJ/kg is assumed, while 60 % of the fuel in the simulation model in this thesis is Refuse Derived Fuels (RDF) with lower carbon-content than coal, thus causing lower fuel-derived CO₂ emissions.

5.2.3 Product CO₂-purity

Table 5.1: CO₂ in flue gas and product purity with different air in-leakage rates

Case no.	1	2	3	4	5
Air in-leakage	2 %	4 %	6 %	8 %	10 %
CO ₂ in flue gas [mol %]	84.85	80.89	77.29	73.99	70.96
Product CO ₂ purity [mol %]	95.08	95.22	95.35	95.44	95.49

Table 5.1 displays the product CO₂ purity with different air in-leakage percentages. The table shows that the product quality actually increases slightly with air in-leakage with this specific CPU design. The CO₂ in the flue gas decreases as would be expected with increasing air in-leakage. The increase in product purity needs to be seen in connection with the CO₂ capture ratio as described below, and is caused by the CPU design.

5.2.4 CO₂ capture ratio

CO₂ captured is the amount of CO₂ captured per tonne clinker produced. CO₂ capture ratio is defined as the fraction of the formed CO₂ which is captured and subsequently stored.

Figure 5.3 displays the CO₂ capture ratio of the oxy-combustion layout with different air in-leakage rates.

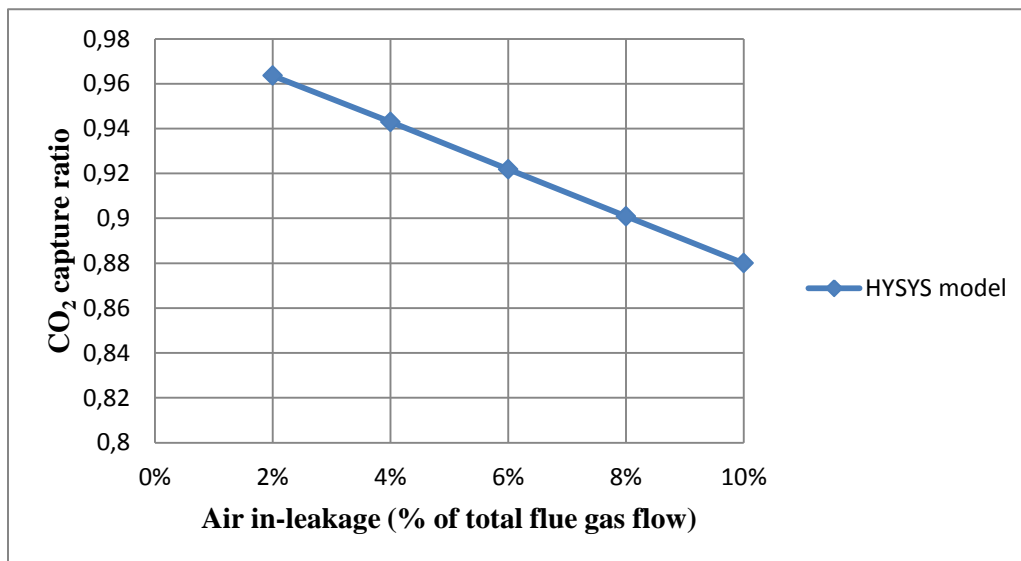


Figure 5.3: CO₂ capture ratio at different air in-leakage rates.

From the figure it can be seen that the CO₂ capture ratio decreases with increased air in-leakage. At an air in-leakage of 10 %, the capture ratio is no longer acceptable according to the design conditions (capture ratio > 0.9). The slope is a decrease of capture ratio of approximately 0.23 per 1 % increase of air in-leakage.

Notice that even though the product purity is higher with increasing air in-leakage, the amount of CO₂ captured and the CO₂ capture efficiency is reduced.

Comparison of CO₂ capture ratio with ECRA (2012)

Figure 6.4 compares the results in Figure 6.3 with results from performance calculations from ECRA, 2012.

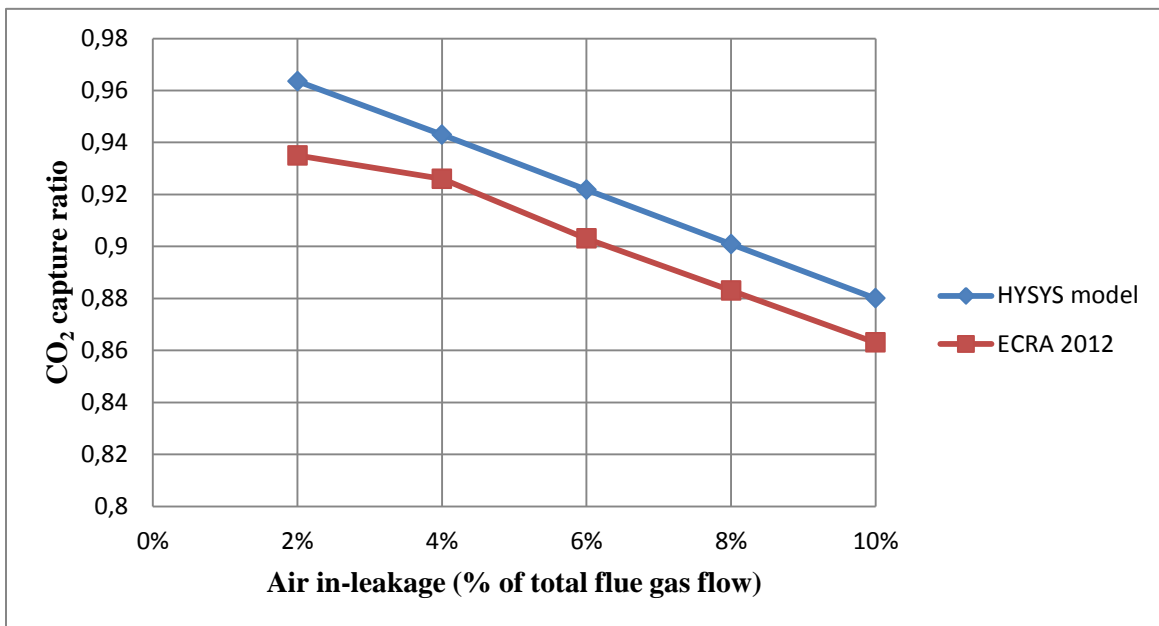


Figure 5.4: Comparison of CO₂ capture ratio with ECRA (2012).

It can be seen that ECRA (2012) achieved similar CO₂ capture ratios to the model in this thesis.

5.2.5 CO₂ avoided

CO₂ avoided is defined as the net reduction of CO₂ emissions per unit of net power output, compared to a reference power plant without CO₂ capture. This oxy-combustion layout requires no additional fuel, only additional electricity for operation of the ASU and the CPU. Compared to other countries in Europe, Norway has a rather unusual distribution of its CO₂ footprint. Norway generates most of its electricity from hydropower, and the specific CO₂ emission from electricity generation is almost negligible. The CO₂ avoided in this case is thus equal to the difference

between CO₂ produced and CO₂ captured, and the CO₂ avoided ratio is equal to the CO₂ capture ratio. Where electricity is generated from fossil fuels, the additional CO₂ emissions have to be taken into account.

5.3 Additional Power Consumption with Oxy-combustion Capture

5.3.1 Power consumption, ASU

The specific energy consumption of the ASU is assumed to be 0.198 kWh/kgO₂.

The actual work per kg ASU output flow is:

$$\frac{0.198 \frac{kWh}{kg O_2} * 32 \frac{kg}{kmol}}{0.95 \frac{kmol O_2}{kmol ASU_{out}}} = \frac{6.669 kWh}{kmol ASU_{out}} * 3600 \frac{s}{h} = 24.01 \frac{MW}{\frac{kmol}{s} from ASU}$$

In the simulations made in this thesis, an oxygen flow of 0.5196 kmol/s from the ASU is assumed, giving a specific energy consumption of 12.48 MW.

The power required by a cryogenic oxygen plant is typically in the range 200-240 kWh/tO₂ in the literature (Barker et al, 2009), so a specific energy consumption of 0.198 kWh/kgO₂ seems to be a reasonable number.

5.3.2 Power Consumption of CPU and ASU with different Air in-leakages

The power consumption of the CPU is highly dependent of the air in-leakage. Assuming an air in-leakage of 6 % of total flue gas flow, which is common at the present cement plants, the specific power is 23.51 MW.

Air in-leakage impacts the power consumption of the CPU. Electricity consumption increases with increasing air in-leakage. As previously stated, the CPU design was chosen to work with different air in-leakages, without having to change the compressor pressure ratio, to be able to compare the results directly.

The energy consumption of the CPU is calculated by summing up the power consumption of the compressors (K-1, K-2 and K-3), the CO₂ pump and the end expander. The gas coolers are assumed to be operated with sea water, and do not require electrical energy.

Table 5.2 shows the results of the sensitivity study.

Table 5.2: Results from sensitivity study

Case no.	1	2	3	4	5
Air in-leakage	2 %	4 %	6 %	8 %	10 %
CO ₂ Captured [kmol/s]	0.8061	0.7888	0.7711	0.7536	0.7361
CO ₂ Captured [t/h]	127.71	124.98	122.18	119.40	116.63
CPU power [MW]	21.26	21.41	23.51	24.61	25.71
CPU power [kWh/t _{CO2}]	166.47	171.30	192.43	206.12	220.44
CPU power increase from reference case	0 %	0.7 %	10.6 %	15.8 %	20.9 %
Energy consumption ASU [MW]	12.48	12.48	12.48	12.48	12.48

The CPU power increase is compared to the reference best case scenario of 2 % air in-leakage. The table shows that the power consumption of the CPU increases with increasing air in-leakage. On average, the power consumption increases with ~2.6 % per percentage of air in-leakage. This is because the increased air in-leakage causes a lower CO₂ concentration in the flue gas, and thus causes a higher work of separation. In addition, higher air in-leakage gives a higher volumetric flow of the flue gas, which also gives higher compression work.

The energy consumption of the ASU remains unchanged, as the air in-leakage only affects the cement plant process and the CPU process.

5.3.3 Comparison with previous studies

Klostermann (2008) reported that the specific energy demand increases by 4.5 % per percentage point of false air. This compares well with the results of this thesis, where the power demand of the CPU increases with 3-5 % per percentage point of air in-leakage.

Performance calculations were conducted by ECRA in 2012. A comparison of the specific power consumption of the modelled oxy-combustion layout with ECRA's performance calculations are displayed in Figure 5.5.

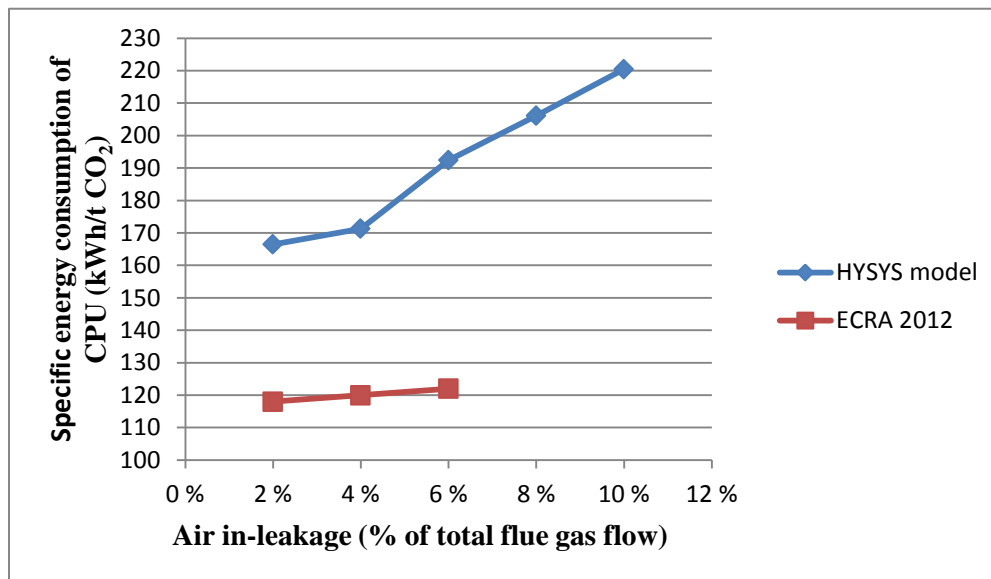


Figure 5.5: Comparison of CPU power consumption with ECRA (2012).

As can be seen from Figure 5.5, the specific power consumption of the CPU modelled is significantly higher than the specific power consumption of the CPU from the ECRA study. This is probably caused by differences in inlet CO₂ concentrations, as well as a different layout of the CPU. The focus of the CPU design in this thesis work has been to achieve the required CO₂ purity, not optimising the power consumption. ECRA (2012) does not specify the process design of the CPU, only that a process design that worked for a wide range of air in-leakage rates was selected. Process conditions were chosen to produce CO₂ at a purity of 95 vol % or greater, while minimizing average unit power (kWh/tonne contained CO₂). However, the sensitivity study performed by ECRA uses a feed CO₂ purity of 91.5 mol % for 2 % air in-leakage, 87.9 mol % for 4 % air in-leakage and 84 mol % for 6 % air in-leakage. This is significantly higher than the comparable feed CO₂ purity from the model studied in this thesis.

Because of these differences, a comparison of percentage increase, as seen in Figure 5.6 is more reasonable. The ECRA 2012 performance calculations are here also compared with the value from Klostermann (4.5 % increase in energy demand per percentage of air in-leakage).

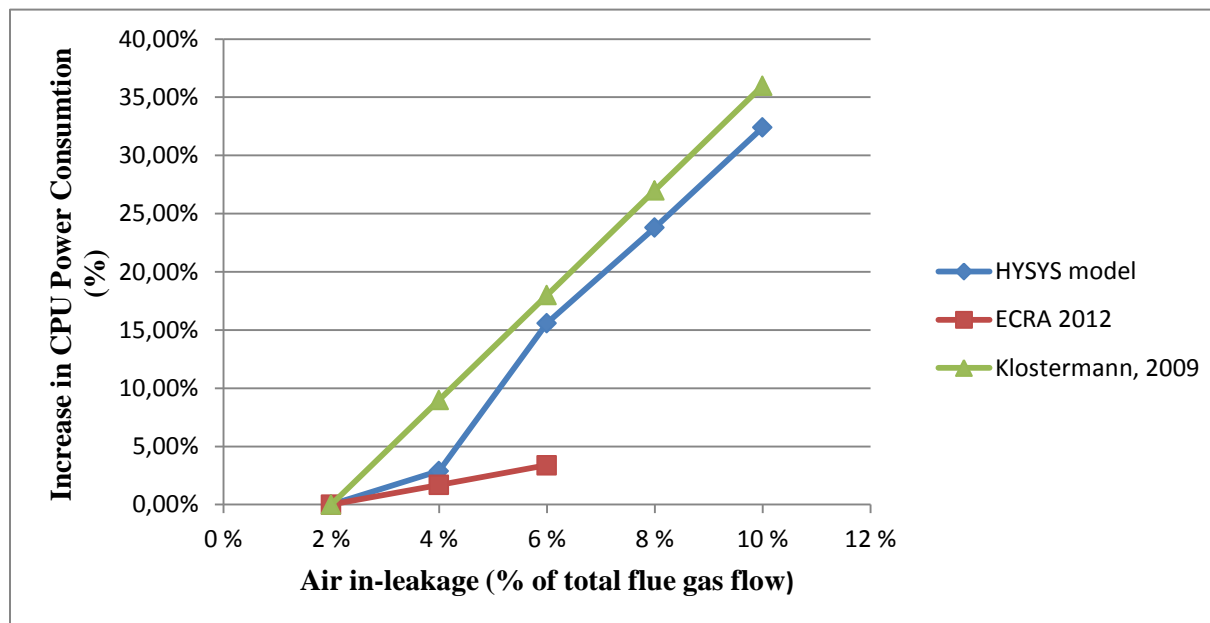


Figure 5.6: Percentage increase in power consumption from CPU per percentage of air in-leakage.

Figure 5.6 still shows significant deviations between the results from this thesis and the performance calculations by ECRA (2012). This thesis has made calculations for a broader range of air in-leakage than ECRA. The HYSYS model curve is not linear. This is probably due to a minor process modification from 2 to 4 %, where the compressor K-2 outlet pressure is changed from 26 bar to 26.5 bar in order to maintain a CO₂ purity of >95 mol%. The percentage increase in CPU energy demand is more comparable to the results from Klostermann (2008).

The energy consumption from the CPU design by ECRA might be too low compared to reality, or the energy consumption from this study and Klostermann might be too high. If installing a CPU on a cement plant, it is important that the energy demand is calculated correctly, to ensure that sufficient amounts of electricity are available from the grid. Also for the prediction of OPEX costs point of view, a too optimistic energy consumption should be avoided. In this case, it is better to use an estimate that is too high, compared to an estimate that is too low. In this work, pressure drop in the piping systems and process units are not considered. In real life, pressure decrease will occur and increase the power consumption for e.g. compression work.

5.4 Conclusion, CPU design and air in-leakage

The simulation results show that it is important that the air in-leakage is controlled and maintained at the lowest achievable level. To achieve the lowest possible energy consumption, the CPU should be specifically designed for the incoming CO₂ purity. This involves changing the pressure in the compressor K-2 and the valve V-101. Large variations in incoming CO₂ purity might result in a CO₂ product with too low quality and a significant increase in electricity consumption.

6 Cement Process Modifications and Operational Risks

6.1 General

The purpose of this chapter is to highlight the results of the literature review concerning process modifications and operational risks for practical implementation of oxy-combustion technologies in the cement production process. This is elaborated in the chapters below. The main conclusions/results indicate the following necessary modifications:

- An Air Separation Unit for production of the oxygen required for the combustion in the kiln and pre-calcliner. In addition, installation of a CO₂ compression and purification unit for processing of the flue gas is required. Additional space for both of these units is necessary.
- For retrofitting of a cement plant, the clinker cooler and the kiln burners requires a new design.
- Reduction of air in-leakages, i.e. by improvement of sealing locations or a waste-gas flushed system.

6.2 Necessary Cement Process Modifications

As mentioned in Chapter 3.2, some additional equipment, such as the ASU and CO₂ CPU, is necessary when implementing the oxy-combustion technology in a cement plant. Sufficient electrical energy supply capacity is also important, as the ASU and CPU causes an increased electricity demand of 15-30 MW. In addition, modification of the existing equipment is necessary.

6.2.1 Optimisation of sealing locations to reduce air in-leakage

The electric energy consumption and costs for oxy-combustion operation are highly dependent on the CO₂ purification unit (CPU), and the air in-leakage becomes an important factor for the CPU performance.

Phase II of ECRA CCS showed that air in-leakage would significantly increase the CO₂ purification and liquefaction costs. As a result, reduction of the intrusion beyond today's levels by optimising the current sealing becomes even more important for overall energy efficiency.

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

Figure 6.1 illustrates the proportional shares of the several sealing locations of the total false air graphically. The result identifies the kiln inlet sealing, the tertiary air (TA) slide damper, pendulum flap boxes, poke holes and specifically the inspection doors in the upper preheater tower as the major contributors to false air intrusion. The inspection doors provide approximately one third of the total false air because of the high differential pressure against which they have to

seal. Accordingly, these identified sealing locations provide the biggest potential for false air reduction.

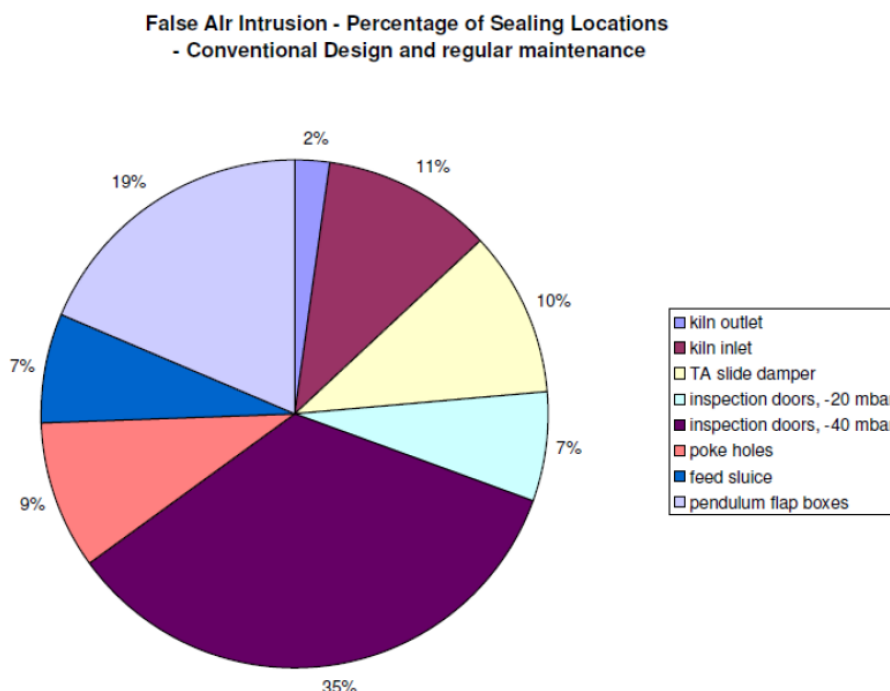


Figure 6.1: Proportional share in total false air ingress of the several sealing locations (ECRA, 2012).

Based on an analysis of the characterisation of the sealing locations, promising options for the development of the optimised sealings were derived by ECRA (2012). Table 6.1 displays the technically recommended optimisation paths for the reduction of false air ingress. The displayed potential (++: high potential, o: low potential, --: not advisable) does not include an economic cost-to-benefit ratio, but shows a mere technical evaluation.

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

Table 6.1: Technical false air reduction potentials for the considered sealing location system (ECRA, 2012)

Sealing location	Function principle			Remark
	Mechanical or geometrical design	Flue gas recirculation	Ambient air suction	
Kiln outlet	+	++	--	Cooling necessary, new design necessary
Kiln inlet	+	++	--	Cooling necessary, new design necessary
TA slide damper	+	++	-	High thermal stress in case of ambient air suction
TA butterfly valves	○	○	○	Mature design, low ingress flow
Poke holes	○	+	++	Cuff/hood around lower calciner duct, CO ₂ -emissions
Feed ports/slucies	○	++	--	No new design necessary, operation of the last handling step process inert
Inspection doors	○	-	-	Mature design, diverse and plant specific locations
Pendulum flap boxes	○	-	+	CO ₂ emissions

Estimation of effectiveness

In order to evaluate the possible optimisation options under a techno-commercial aspect, the estimation was outlined as a comparison of four scenarios (ECRA, 2012):

1. **Reference case:** Conventional sealing solutions in a realistic state of maintenance after several years of operation
2. **Optimum maintenance:** All sealing locations are equipped with the best possible mechanical design, best practice erection and optimised maintenance (gap width reduction 50 %)
3. **Improved maintenance:** With a more realistic improvement rate (gap width reduction 25 %)
4. **Waste gas flushed:** All optimised sealings and additionally all singular sealing locations equipped with waste gas-flushed or ambient air suction technologies (kiln inlet, kiln outlet, tertiary air side damper, feed sluice)

Figure 6.2 shows the comparison of the four scenarios regarding their air in-leakage. The reference case displays a total amount of approximately 14 % air in-leakage related to the total exhaust gas after leaving the preheater. This amount may seem rather high for new plants, but reflects the addition of many small spots of un-tightness which may occur through the course of time of operation. The value serves as a reference for the improvement options covered by the other scenarios.

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

Scenario 3 “Improved Maintenance” also displays a considerable reduction of air in-leakage down to approximately 6 %. This corresponds to a reduction of all gap heights by 25 % of their initial height. This seems to be an achievable scenario.

Scenario 4 “Waste Gas Flushed” results in only 1 % of air in-leakage into the process gas. The main contributors are the inspection doors at high pressure differentials.

Scenario 4 offers the lowest air in-leakage percentage. However, it also requires the highest investment costs, as the waste gas-flushed sealings have to be supplied with the respective gas through long ducts. In total, investment costs of at least € 250,000 should be considered for the supply of waste gas to the 4 sealing locations.

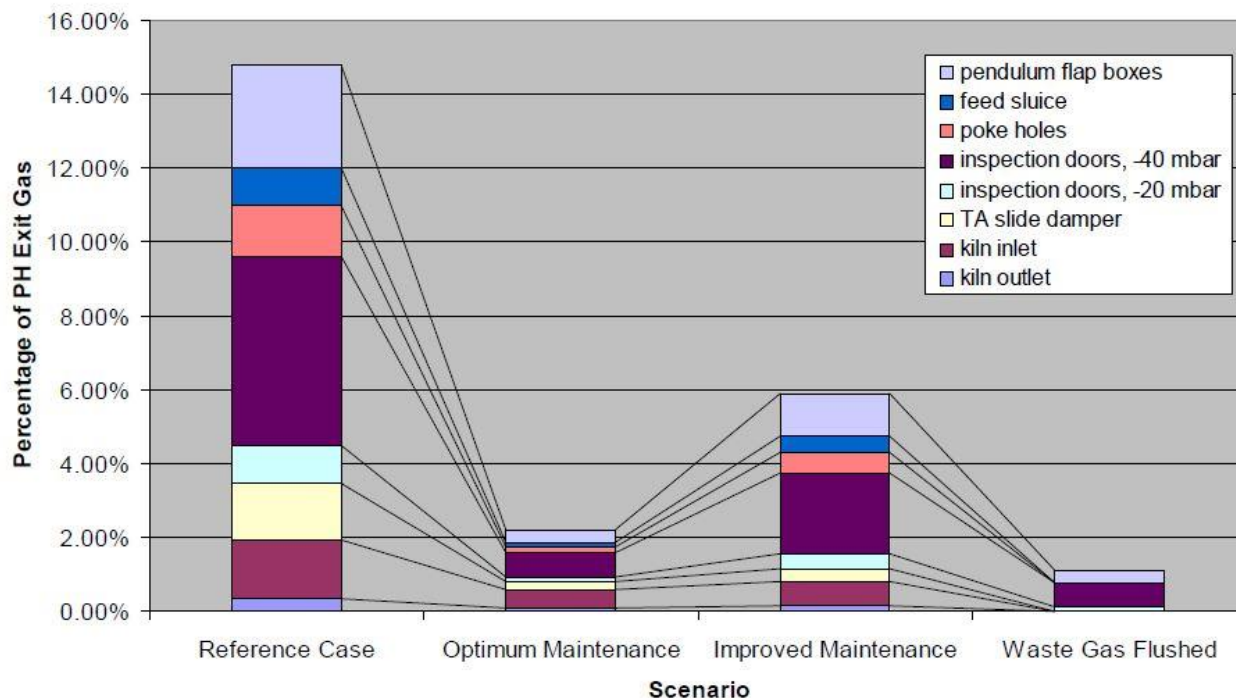


Figure 6.2: Comparison of different scenarios for the reduction of false air ingress (ECRA, 2012).

The major contributors to air in-leakage are the inspection doors, poke holes and pendulum flap box covers, mostly working at high differential pressures. The number of these components and their plant-specific positions do not facilitate the application of waste gas flushed technologies. However, by adherence to high quality design and fabrication of these components, the air in-leakage can be kept below 6 %. With dedicated efforts in maintenance, air in-leakage as low as 3 % seems to be achievable without applying waste gas recirculation.

6.2.2 Burner Design

Oxy-combustion operation requires an adaption of the burner design to establish flame characteristics comparable to those under conventional condition. A burner design for oxy-combustion operation has to take into account both the characteristics of high oxygen concentration as well as CO_2 in the combustion air. An optimum burner operation should prevent damaging effects to the refractory or over-burning of the clinker.

6.2.3 Two-staged Clinker Cooler

The oxy-combustion plant design chosen as the best design by ECRA (2009) requires a two-staged clinker cooler. The required gas-tightness of the two stages, which are operated with different gas atmospheres, could be matched by two possible design concepts. Both concepts rely on the separation of the stage by dynamic devices in the hot clinker zone. With reference to a

potential retrofit plant, a concept using two heat shields has been selected by ECRA as the most promising solution. It has emerged that even existing coolers could be modified with respect to two compartments separated by a separating flap between the part cooled by recycled CO₂ and the other being cooled by ambient air.

6.3 Operational Risks

ECRA (2012) addresses several safety aspects that need to be taken into account when operating a cement plant with oxy-combustion technology:

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

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

In general more safety and controlling devices have to be installed under oxy-combustion operation and the personnel have to be instructed and thoroughly trained to understand and control the increased risks.

6.3.1 Impact of Oxy-combustion on Product Quality

Combustion of fuels with pure oxygen in combination with recycling of flue gas to moderate the temperature profile causes both the material conversion in the kiln system and the operational specifications of the overall process to be different from those in conventional kiln operations. However, research performed in Phase III of the ECRA CCS Project showed that the negative impacts of oxy-combustion on the product quality seem to be negligible: Different clinkers were burned under oxy-combustion conditions in a laboratory oven and were used for the production of cement samples. The testing of the cement characteristics showed only slight variances (below 3 %) in properties such as strength development and compressive strength compared to standard cement (ECRA, 2012). This is promising with respect to implementation of the technology.

6.3.2 Durability of refractory materials

Another parameter investigated in the ECRA CCS Project – Phase III, was the durability of basic and non-basic refractory material under oxy-combustion conditions, with respect to the temperature profile and gas atmosphere in an oxy-combustion kiln. The experiments showed that brickwork consistent with basic material withstood the modified burning atmosphere, while the non-basic material showed a higher degree of thermo-chemical attack during oxy-combustion treatment. Further operation tests should be performed, as durability of refractory materials will have substantial effect on operational cost (OPEX), operating hours and operational risks.

7 Conclusions and Suggestions for Further Work

In this thesis, a process simulation model was built in Aspen HYSYS, and the impact of air in-leakage on the cement process and on the CO₂ capture process was investigated. It was found that air in-leakages in the cement plant influences the CO₂ concentration of the flue gas from the cement plant and the energy consumption of the CPU. Air in-leakage should be kept to a minimum to ensure effective CO₂ capture.

Evaluations of the electricity consumption of oxy-combustion technologies identified the CO₂ compression and purification unit (CPU) as a major consumer. Depending on the flue gas conditions, i.e. volume flow, composition, temperature etc., the percentage of air in-leakage becomes an important factor for the CPU performance. Simulations from HYSYS, as well as research from ECRA (2012), showed that the CPU performance decreases with increasing air in-leakage, as well as an increase in electricity consumption.

Air in-leakage could be significantly reduced by using complex solutions such as waste gas flushed and suction-based systems. Based on the localisation of the main air in-leakages (poke holes, inspection doors, etc.), an improved maintenance of these devices was identified as a sufficient measure in terms of improving CPU performance.

A literature review on necessary cement process modifications and operational risks has been conducted. The essential issue of constant product quality was proven in laboratory tests by ECRA (2012). Different clinkers were burned under oxy-combustion conditions in a laboratory oven and were used for the production of cement samples. Testing of the cement characteristics resulted in only slight variances (below 3 %) in properties such as strength development and compressive strength compared to standard cements. Hence, negative impact of oxy-combustion on the product quality seems to be negligible.

The durability of basic and non-basic refractory material under oxy-combustion conditions was investigated by ECRA (2012). Brickwork consisting of basic material withstood the changed burning atmosphere, while the non-basic material showed a higher degree of thermo-chemical attack during oxy-combustion treatment.

With respect to burner design, research by ECRA (2012) showed that switching from conventional conditions to oxy-combustion conditions without adaption of the burner design would result in significant changes in the clinker quality due to a flame on a lower temperature level and higher gas velocities. However, adjusting the burner design and the associated parameters to the oxy-combustion conditions could re-establish flame characteristics comparable to those of conventional conditions. Testing of such burners in practical applications is important to verify this.

A notable feature of the plant layout considered in this thesis and by ECRA (2012) is the two-stage clinker cooler. The required gas-tightness of the two stages, which are operated with

different gas atmospheres, could be matched by two possible design concepts. Both concepts rely on the separation of the stages by dynamic devices in the hot clinker zone. With reference to a potential retrofit plant, a concept using two heat shields was selected as the most promising solution.

In general, only a few modifications of the cement plant technology have to be implemented, and the necessary redesign of plant components (cooler and burner) does not set limits for the retrofitting. A prerequisite of the retrofitting is sufficient space in the surroundings of the plant to install the ASU and the CPU. The conventional way of operating a cement plant does not have to be completely adapted. In conclusion, the operation of an oxy-combustion cement plant would not differ completely from that of a conventional plant.

Oxy-combustion technologies still requires more research, even if it could be shown that it might be applicable at existing kilns, however not without major investments. Although the technology might be less expensive than post-combustion, the overall cost due to the investment for modification and the high energy cost once in operation leave the economic impact of CCS on the cement industry still open.

Today, CO₂ capture technologies for the cement industry are not technically available. Oxy-combustion capture is state-of-the-art in a few other industry sectors, and seems to be promising for new kilns. However, from today's point of view, CCS is far too expensive for the cement industry, and more research is needed. ECRA's ongoing research project is in its fourth phase, and the project goal is to enable the cement industry to give scientifically based reliable answers to political requirements in the future.

For future work, further optimization of the ASU and the CPU should be studied, including optimizing the required oxygen supply from the ASU to the cement plant. It should be investigated if the combustion with oxygen instead of air causes a reduction in fuel consumption. Further research on the oxy-combustion cement process is necessary to be able to commercialize the technology. Limits to oxygen and CO₂ concentrations in kiln and pre-calciner are required to model the process with minimum influence on the cement process. Economical technical solutions for the necessary process plant modifications are needed.

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Appendices

Appendix A	HYSYS Simulation Model	A-1
	Figure A.1: Process Flow Diagram	A-1
	Table A.1: HYSYS Material Streams and Compositions	A-3
	Table A.2: Heat Flows.....	A-6
Appendix B	Sensitivity Analysis Results.....	B-1
Appendix C	Performance calculations summary of effect of air in-leakage on the CPU Performance (ECRA, 2012).....	C-1

Appendix A HYSYS Simulation Model

Figure A.1: Process Flow Diagram

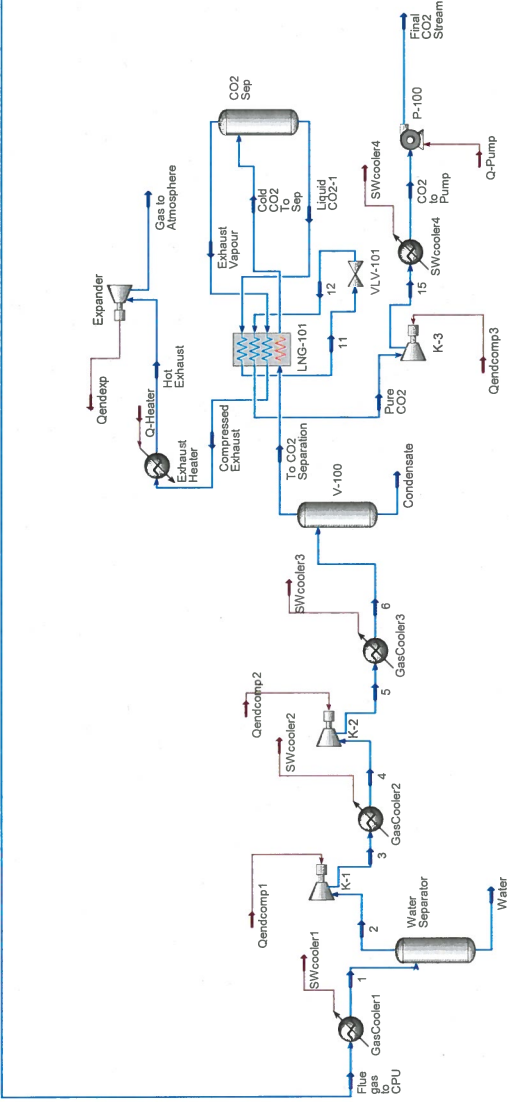
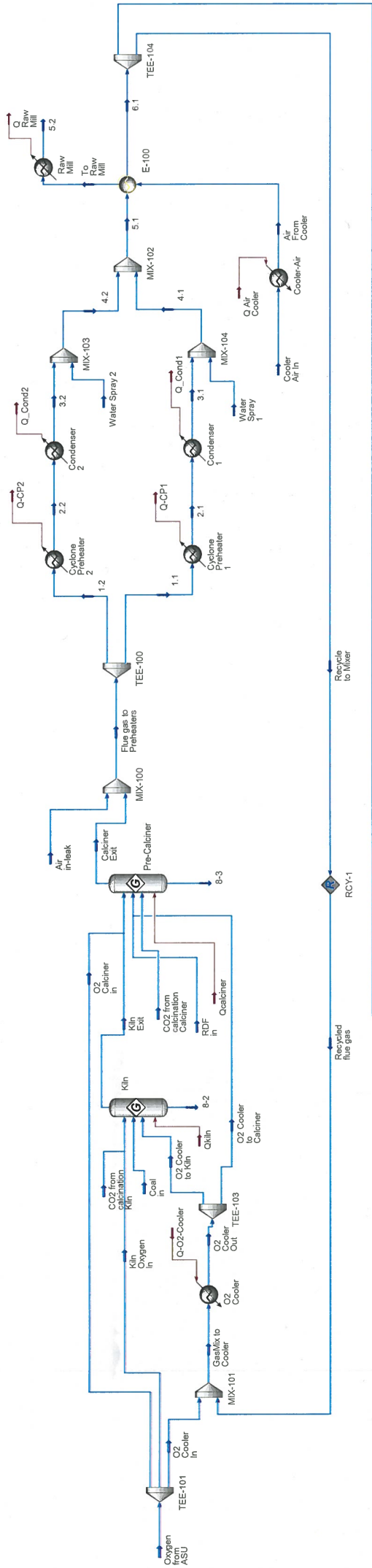


Table A.1: HYSYS Material Streams and Compositions

Stream name	1	1.1	1.2	2	2.1	2.2	3	3.1	3.2	4
Vapour Fraction	0,6556	1	1	1	1	1	1	1	1	1
Temperature [C]	20,00	944,79	944,79	20,00	381,00	382,00	313,27	169,00	224,00	72,48
Pressure [bar]	0,953	1,013	1,013	0,953	1,013	1,013	15,953	1,013	1,013	15,953
Molar Flow [kgmole/s]	1,5040	1,3538	1,3538	0,9860	1,3538	1,3538	0,9860	1,3538	1,3538	0,9860
Mass Flow [kg/h]	1,82E+05	1,72E+05	1,72E+05	1,48E+05	1,72E+05	1,72E+05	1,48E+05	1,72E+05	1,72E+05	1,48E+05
Liquid Volume Flow [m3/h]	209,73	199,97	199,97	176,07	199,97	199,97	176,07	199,97	199,97	176,07
Heat Flow [MW]	-483,87	-369,32	-369,32	-335,73	-405,37	-405,31	-324,15	-417,18	-414,23	-334,22
Composition (mol fraction)										
Mol Frac (N2)	0,0335	0,0372	0,0372	0,0510	0,0372	0,0372	0,0510	0,0372	0,0372	0,0510
Mol Frac (O2)	0,0385	0,0428	0,0428	0,0587	0,0428	0,0428	0,0587	0,0428	0,0428	0,0587
Mol Frac (Argon)	0,0106	0,0118	0,0118	0,0162	0,0118	0,0118	0,0162	0,0118	0,0118	0,0162
Mol Frac (CO2)	0,5562	0,6180	0,6180	0,8485	0,6180	0,6180	0,8485	0,6180	0,6180	0,8485
Mol Frac (H2)	0	0	0	0	0	0	0	0	0	0
Mol Frac (CO)	8,86E-08	9,85E-08	9,85E-08	1,35E-07	9,85E-08	9,85E-08	1,35E-07	9,85E-08	9,85E-08	1,35E-07
Mol Frac (H2O)	0,3611	0,2902	0,2902	0,0255	0,2902	0,2902	0,0255	0,2902	0,2902	0,0255
Stream name	4.1.	4.2.	5	5.1.	5.2	6	6.1	8-2	8-3	11
Vapour Fraction	1	1	1	1	1	0,9758	1	0	0	9,55E-03
Temperature [C]	168,99	223,99	123,32	196,26	97,62	20,00	171,18	1025	955	-45
Pressure [bar]	1,013	1,013	26,5	1,013	1,013	26,5	1,013	1,013	1,013	26,5
Molar Flow [kgmole/s]	1,5291	1,4790	0,9860	3,0080	4,3380	0,9860	3,0080	0,0000	0,0000	0,8478
Mass Flow [kg/h]	1,83E+05	1,80E+05	1,48E+05	3,64E+05	4,51E+05	1,48E+05	3,64E+05	0	0	1,32E+05
Liquid Volume Flow [m3/h]	211,36	208,11	176,07	419,47	520,83	176,07	419,47	0	0	159,25
Heat Flow [MW]	-458,71	-443,65	-332,41	-902,36	9,23	-337,76	-905,30	0	0	-332,48
Composition (mol fraction)										
Mol Frac (N2)	0,0329	0,0340	0,0510	0,0335	0,7900	0,0510	0,0335	0,0236	0,0240	0,0156
Mol Frac (O2)	0,0379	0,0392	0,0587	0,0385	0,2100	0,0587	0,0385	0,0101	0,0398	0,0238
Mol Frac (Argon)	0,0105	0,0108	0,0162	0,0106	0,0000	0,0162	0,0106	0,0125	0,0119	0,0083
Mol Frac (CO2)	0,5471	0,5657	0,8485	0,5562	0,0000	0,8485	0,5562	0,6815	0,6289	0,9508
Mol Frac (H2)	0	0	0	0	0	0	0	0	0	0
Mol Frac (CO)	8,72E-08	9,01E-08	1,35E-07	8,86E-08	0,00E+00	1,35E-07	8,86E-08	9,55E-07	1,00E-07	3,47E-08
Mol Frac (Carbon)	0	0	0	0	0	0	0	1,00E-45	1,00E-45	0,00E+00
Mol Frac (H2O)	0,3716	0,3503	0,0255	0,3611	0,0000	0,0255	0,3611	0,2722	0,2954	0,0015

Stream name	12	15	Air From Cooler	Air in-leak	Calciner Exit	CO2 from calc. Calciner	CO2 from calc. to Kiln	CO2 to Pump	Coal in	Cold CO2 to Sep.
Vapour Fraction	0,1119	1	1	1	1	1	1	0	0,3107	0,1189
Temperature [C]	-55,81	227,74	277,98	15,00	955,00	1025,00	1025,00	20,93	9,00	-54,00
Pressure [bar]	8,5	74	1,013	1,013249966	1,013	1,013	1,013	74	1,013	26,5
Molar Flow [kgmole/s]	0,8478	0,8478	4,3380	0,0470	2,6606	0,3000	0,1500	0,8478	0,2239	0,9621
Mass Flow [kg/h]	1,32E+05	1,32E+05	4,51E+05	4,90E+03	3,39E+05	4,75E+04	2,38E+04	1,32E+05	7,94E+03	1,47E+05
Liq. Volume Flow [m3/h]	159,25	159,25	520,83	5,63	394,31	57,59	28,79	159,25	11,29	174,52
Heat Flow [MW]	-332,48	-311,69	32,84	-0,01	-738,63	-103,24	-51,62	-325,49	-0,05	-345,63
Composition (mol frac.)										
Mol Frac (N2)	0,0156	1,56E-02	1	0,7810	2,40E-02	0,00E+00	0	1,56E-02	3,94E-03	5,23E-02
Mol Frac (O2)	0,0238	2,38E-02	0	0,2100	3,98E-02	0,00E+00	0	2,38E-02	2,82E-02	6,02E-02
Mol Frac (Argon)	0,0083	8,26E-03	0	0,0090	1,19E-02	0,00E+00	0	8,26E-03	0,00E+00	1,66E-02
Mol Frac (CO2)	0,95080	0,95080	0	0,00000	0,62888	1,00000	1,00000	0,95080	0,00000	0,86949
Mol Frac (H2)	0	9,71E-10	0	0	3,14E-08	0,00E+00	0	9,71E-10	2,79E-01	4,34E-08
Mol Frac (CO)	0	3,47E-08	0	0	1,00E-07	0,00E+00	0	3,47E-08	0,00E+00	1,39E-07
Mol Frac (Carbon)	0	0	0	0	0	0	0	0	0,6893	0
Mol Frac (H2O)	1,53E-03	1,53E-03	0	0	2,95E-01	0	0	1,53E-03	0,00E+00	1,35E-03
Stream name										
Vapour Fraction	1	0	1	1	1	1	1	1	1	1
Temperature [C]	18,00	20,00	9,00	-54,00	30,08	171,18	944,79	56,97	141,55	300,00
Pressure [bar]	26,5	26,5	1,013	26,5	110	1,013	1,013	1,013	1,013	26,5
Molar Flow [kgmole/s]	0,1144	0,0239	4,3380	0,1144	0,8478	1,5040	2,7076	0,1144	1,9626	0,1144
Mass Flow [kg/h]	1,42E+04	1,55E+03	4,51E+05	1,42E+04	1,32E+05	1,82E+05	3,44E+05	1,42E+04	2,35E+05	1,42E+04
Liq. Volume Flow [m3/h]	15,26	1,55	520,83	15,26	159,25	209,73	399,95	15,26	256,45	15,26
Heat Flow [MW]	-12,09	-6,83	-2,06	-12,37	-325,23	-452,65	-738,65	-11,90	-452,80	-11,00
Composition (mol frac.)										
Mol Frac (N2)	0,3244	0	0,7900	0,3244	0,0156	0,0335	0,0372	0,3244	0,0303	0,3244
Mol Frac (O2)	0,3301	0	0,2100	0,3301	0,0238	0,0385	0,0428	0,3301	0,2515	0,3301
Mol Frac (Argon)	0,0788	0	0,0000	0,0788	0,0083	0,0106	0,0118	0,0788	0,0152	0,0788
Mol Frac (CO2)	0,2668	0,0009	0,0000	0,2668	0,9508	0,5562	0,6180	0,2668	0,4263	0,2668
Mol Frac (H2)	0	0	0	0	0	0	0	0	0	0
Mol Frac (CO)	0	0	0	0	0	0	0	0	0	0
Mol Frac (Carbon)	0	0	0	0	0	0	0	0	0	0
Mol Frac (H2O)	0	0,9991	0,0000	0,0000	0,0015	0,3611	0,2902	0,0000	0,2767	0,0000

Stream name	Kiln Exit	Kiln Oxygen In	Liquid CO2-1	O2 Calciner in	O2 Cooler In	O2 Cooler Out	O2 Cooler to Calciner	O2 Cooler to Kiln	Oxygen from ASU	Pure CO2
Vapour Fraction	1	1	0	1	1	1	1	1	1	0,9994
Temperature [C]	1025	15	-54	15	15	999	999	999	15	-0,20
Pressure [bar]	1,013	1,013	26,5	1,013	1,013	1,013	1,013	1,013	1,013	7,5
Molar Flow [kgmole/s]	0,7946	0,0498	0,8478	0,0112	0,4586	1,9626	1,4062	0,5564	0,5196	0,8478
Mass Flow [kg/h]	1,04E+05	5,77E+03	1,32E+05	1,30E+03	5,31E+04	2,35E+05	1,68E+05	6,66E+04	6,02E+04	1,32E+05
Liq. Volume Flow [m3/h]	122,22	5,07	159,25	1,14	46,71	256,45	183,75	72,70	52,92	159,25
Heat Flow [MW]	-229,19	-0,01	-333,26	0,00	-0,14	-381,61	-273,42	-108,19	-0,16	-318,84
Composition (mol frac.)										
Mol Frac (N2)	0,0236	0,0200	0,0156	0,0200	0,0200	0,0303	0,0303	0,0303	0,0200	0,0156
Mol Frac (O2)	0,0101	0,9500	0,0238	0,9500	0,9500	0,2515	0,2515	0,2515	0,9500	0,0238
Mol Frac (Argon)	0,0125	0,0300	0,0083	0,0300	0,0300	0,0152	0,0152	0,0152	0,0300	0,0083
Mol Frac (CO2)	0,6815	0	0,9508	0	0	0,4263	0,4263	0,4263	0	0,9508
Mol Frac (H2)	2,14E-07	0	9,71E-10	0	0	2,12E-08	2,12E-08	2,12E-08	0	9,71E-10
Mol Frac (CO)	9,55E-07	0	3,47E-08	0	0	6,79E-08	6,79E-08	6,79E-08	0	3,47E-08
Mol Frac (Carbon)	0	0	0	0	0	0	0	0	0	0
Mol Frac (H2O)	0,2722	0	1,53E-03	0	0	0,2767	2,77E-01	0,2767	0	1,53E-03
Stream name										
	RDF in	Recycle to Mixer	Recycled flue gas	To CO2 Separation	To Raw Mill	Water Out	Water Spray 1	Water Spray 2		
Vapour Fraction	0,5071	1	1	1	1	0	1	1		
Temperature [C]	9,00	171,18	171,18	20,00	300,00	20,00	169,00	224,00		
Pressure [bar]	1,013	1,013	1,013	26,5	1,013	0,953	1,013	1,013		
Molar Flow [kgmole/s]	0,4710	1,5040	1,5040	0,9621	4,3380	0,5180	0,1753	0,1252		
Mass Flow [kg/h]	1,80E+04	1,82E+05	1,82E+05	1,47E+05	4,51E+05	3,36E+04	1,14E+04	8,12E+03		
Liq. Volume Flow [m3/h]	30,83	209,73	209,75	174,52	520,83	33,67	11,39	8,13		
Heat Flow [MW]	-0,14	-452,65	-452,66	-330,93	35,78	-148,14	-41,53	-29,42		
Composition (mol frac.)										
Mol Frac (N2)	0,0050	0,0335	0,0335	0,0523	0,79	5,15E-08	0	0		
Mol Frac (O2)	0,1190	0,0385	0,0385	0,0602	0,21	1,60E-07	0	0		
Mol Frac (Argon)	0	0,0106	0,0106	0,0166	0	6,70E-10	0	0		
Mol Frac (CO2)	0	0,5562	0,5563	0,8695	0	3,65E-05	0	0		
Mol Frac (H2)	0,3831	2,77E-08	2,77E-08	4,34E-08	0	2,88E-16	0	0		
Mol Frac (CO)	0	8,86E-08	8,86E-08	1,39E-07	0	7,84E-14	0	0		
Mol Frac (Carbon)	0,4929	0	0	0	0	0	0	0		
Mol Frac (H2O)	0	0,3611	0,3611	1,35E-03	0	0,99996	1	1		

Table A.2: Heat Flows

Air in-leakage	Name	Q Air Cooler	Q Raw Mill	Q-CP1	Q-CP2	Q-Heater
2 %	Heat Flow [MW]	34,900	26,550	36,044	35,986	1,088
4 %	Heat Flow [MW]	34,900	26,550	36,225	36,165	1,724
6 %	Heat Flow [MW]	34,900	26,550	36,406	36,344	2,368
8 %	Heat Flow [MW]	34,900	26,550	36,587	36,524	3,006
10 %	Heat Flow [MW]	34,900	26,550	36,768	36,703	3,641
Air in-leakage	Name	Q-O2-Cooler	Q-Pump	Q_Cond1	Q_Cond2	Qcalciner
2 %	Heat Flow [MW]	71,187	0,266	11,815	8,919	-132,639
4 %	Heat Flow [MW]	72,404	0,261	12,120	9,148	-132,721
6 %	Heat Flow [MW]	73,621	0,256	12,425	9,376	-132,803
8 %	Heat Flow [MW]	74,838	0,250	12,730	9,605	-132,885
10 %	Heat Flow [MW]	76,054	0,245	13,034	9,833	-132,967
Air in-leakage	Name	Qendcomp1	Qendcomp2	Qendcomp3	Qendexp	Qkiln
2 %	Heat Flow [MW]	11,578	1,806	6,704	0,904	-69,320
4 %	Heat Flow [MW]	12,193	1,976	6,549	1,435	-69,308
6 %	Heat Flow [MW]	12,809	2,076	6,406	1,968	-69,296
8 %	Heat Flow [MW]	13,425	2,175	6,267	2,496	-69,285
10 %	Heat Flow [MW]	14,043	2,275	6,129	3,022	-69,273
Air in-leakage	Name	SWcooler1	SWcooler2	SWcooler3	SWcooler4	
2 %	Heat Flow [MW]	31,227	10,063	5,343	13,351	
4 %	Heat Flow [MW]	31,419	10,601	5,653	13,043	
6 %	Heat Flow [MW]	31,611	11,140	5,873	12,743	
8 %	Heat Flow [MW]	31,803	11,681	6,095	12,459	
10 %	Heat Flow [MW]	31,995	12,223	6,317	12,184	

Appendix B Sensitivity Analysis Results

Case no.	1	2	3	4	5
Air in-leakage	2 %	4 %	6 %	8 %	10 %
CO ₂ in flue gas [mol %]	84.85	80.89	77.29	73.99	70.96
Product CO ₂ purity [mol %]	95,08	95,22	95,35	95,44	95,49
CO ₂ Captured [kmol/s]	0,8061	0,7888	0,7711	0,7536	0,7361
CO ₂ captured [t/h]	127,70	124,98	122,18	119,40	116,63
CO ₂ in flue gas [kmol/s]	0,8366	0,8365	0,8365	0,8365	0,8365
CO ₂ Capture efficiency [%]	96,35	94,30	92,19	90,09	88,00
CPU power [MW]	21,26	21,41	23,51	24,61	25,71
CPU power [kWh/tCO ₂]	166,47	171,30	192,43	206,12	220,44
Energy consumption ASU [MW]	12,48	12,48	12,48	12,48	12,48

Appendix C Performance calculations summary of effect of air in-leakage on the CPU Performance (ECRA, 2012)

Case No.	1	2	3	4
Air intrusion	2 %	4 %	6 %	6 %
Type of CPU	Partial Con- densation	Partial Con- densation	Partial Con- densation	Distillation
Feed CO ₂ purity (dry), mol %	91.5	87.9	84.0	84.0
Product CO ₂ purity, mol %	95.8	95.2	95.0	99.9
CO ₂ capture efficiency, %	93.5	92.6	90.3	90.0
CO ₂ captured, t/d	2,353	2,320	2,255	2,248
CPU power, kWh/t _{CO2}	118	120	122	133
Steam, kg/h	1,796	2,503	3,645	4,037
Cooling water, m ³ /h	1,318	1,360	1,387	1,496
Process water, m ³ /h	0.78	0.80	0.84	0.84
Process condensate, m ³ /h	0.41	0.43	0.45	0.45
Acid waste, m ³ /h	0.87	0.90	0.93	0.93