Process integration of CO_2 capture by means of calcium looping technology

Master's thesis in Sustainable Energy Systems programme

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MASTER'S THESIS

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Abstract

Carbon capture and storage (CCS) can play a significant role in the attempt to mitigate climate change. Among the technologies today available for CO_2 capture, calcium looping exploits the reaction that takes place at medium temperatures between lime (CaO) and CO_2 to form limestone ($CaCO_3$) which can be reversed at higher temperatures to release pure CO_2. The process is based on well-known technology but its application for CO_2 capture has been suggested only recently and is less established than other CO_2 capture technologies such as chemical absorption using amines or ammonia as solvents. A reason for this is that fuel is needed to provide high temperature heat. Thus carbon capture by calcium looping can represent a competitive solution where fuel is available in large quantities like in coal power plants. In addition, since a certain quantity of spent sorbent is obtained from the calcium looping, an interesting application arises when this spent lime can be further used for other purposes. This is the case of the cement industry where lime from the calcium looping can reduce the demand of fresh limestone and the energy consumption for its calcination into lime. The aim of this thesis is to investigate the process integration opportunities of carbon capture by the calcium looping technology mainly from a thermodynamic point of view and for the two most relevant application cases: coal power plant and cement industry. Pinch analysis is used as a tool for estimating the consequences of calcium looping application on the process heat and power balances under ideal heat recovery conditions. For this purpose, process modelling and simulation is conducted to obtain temperature and heat load information of the different system parts.

The work is organised in two parts discussing the integration aspects of calcium looping with a state of the art coal power plant and a combined power and cement production plant respectively. Three configurations are considered for integration of calcium looping with the coal power plant: two cases assuming a separate steam cycle to recover the excess heat from the calcium looping process (each case with different complexity of the steam cycle) and one case where heat from the coal plant and calcium looping process are recovered and used in the same steam cycle. To assess the integration effect of carbon capture the penalty on the power plant thermal efficiency is used as an indicator. For comparison oxy-fuel coal combustion technology and subsequent CO_2 separation by water condensation is also investigated. The case where calcium looping and the coal power plant are integrated with the same steam cycle achieves the best result in terms of electrical efficiency, with a penalty of 5.3%-points compared to a reference coal plant without calcium looping (from 42.8% to 37.5%). The analysis of integration between coal power plant, cement production plant and calcium

looping is conducted considering two cases: the first where the cement plant output is kept equal to the reference plant, and the second where the cement output is adjusted to completely replace the limestone input with the spent sorbent from the calcium looping. The integration effects are assessed considering different indicators, such as the thermal efficiency penalty with respect the reference power plant, the specific fuel consumption for cement production, the reduction in specific GHG-emissions from the combined cement and power production. In the case of limestone free cement production the further integration of cement production with coal power plant and calcium looping contributes to a minor reduction in thermal efficiency (from 37.5% to 37.3%).

Sammanfattning

Koldioxidavskiljning och lagring (CCS) kan spela en signifikant roll i att försöka mildra effekterna av klimatförändringarna. Bland de teknologier som idag finns tillgängliga för CO_2 avskiljning, utnyttjar ”Kalciumlooping” den reaktion som sker vid medelhöga temperaturer mellan kalk (CaO) och CO_2 för att forma kalksten ($CaCO_3$), vilken sedan kan reverseras vid högre temperaturer för att frigöra ren CO_2. Processen är baserad på välkänd teknologi, men är mer nyligen föreslagen och därmed inte lika etablerad som annan koldioxidavskiljningsteknologi som kemisk absorption med hjälp av amin eller ammoniak som lösningsmedel. En anledning för detta är att bränsle behövs för att tillföra höggradig värme. På detta sätt kan koldioxidavskiljning genom kalciumlooping representera en konkurrenskraftig där bränsle finns tillgängligt i stora kvantiteter som i kolkraftverk. Ytterligare, sedan en viss mängd av utrensat sorbentmaterial erhålls från kalciumloopingsprocessen, uppstår en intressant applikation när denna utrensade kalk vidare kan användas för andra ändamål. Detta är fallet för cement industrin där kalk från kalciumloopingsprocessen kan reducera både behovet av färsk kalksten och energikonsumtionen för dess kalcination till kalk. Målet med detta examensarbete är att undersöka processintegrationsmöjligheterna för koldioxidsavskiljning genom kalciumloopingsteknologi, främst från en termodynamisk synvinkel och för de två mest relevanta applikationerna: kolkraftverk och cementindustri. Pinchanalys används som ett hjälpmedel för att uppskatta konsekvenserna av kalciumloopingsapplikation på processvärme och kraftbalanser under ideala värmeåtervinningsförhållanden. I detta syfte, utförs processmodellering och simulation för att erhålla temperatur och värmelast information för de olika systemdelarna.

Arbetet är organiserat i två delar som behandlar integrationsaspekterna av kalciumlooping med ett toppmodernt kolkraftverk och en kombinerad kraft- och cementproduktionsanläggning respektive. Tre konfigurationer övervägs för integration av kalciumlooping med kolkraftverket: två fall som antar en separat ångcykel för att återvinna överskottsvärmen från kalciumloopingsprocessen (med olika komplexitet på ångcykeln för respektive fall) och ett fall där värme från kolkraftverket och kalciumloopingsprocessen återvinns och används i samma ångcykel. För att utvärdera integrationseffekten av koldioxidsavskiljning så används effekten på kraftverkets termiska verkningsgrad som en indikator. För jämförelse undersöks också oxy-fuel kolförbränning med efterföljande CO_2

avskiljning som ett alternativ för koldioxidsavskiljning för kolkraftverket. Det fall där kalciumlooping och kolkraftverket är integrerade i samma ångcykel uppnår det bästa resultatet sett till elektrisk effektivitet, med ett effektivitetsfall på 5.3%-enheter jämfört med ett referens kolkraftverk utan kalciumlooping (från 42.8 % till 37.5%). Analysen av integrationen mellan kolkraftverk, cementproduktionsanläggning och kalciumlooping utförs med avseende på två fall: det första där cementanläggningens produktion hålls lika med referensanläggningen, och ett andra där cementproduktionen justeras för att helt ersätta kalkstensinputen med det utrensade sorbentmaterialet från kalciumloopingsprocessen. Integrationseffekterna utvärderas med avseende på olika faktorer, så som det termiska verkningsgradsstraffet jämfört med referens kraftverket, den specifika bränslekonsumtionen för cementproduktion, reduceringen av specifika växthusgasutsläpp från den kombinerade cement- och kraftproduktionen. I fallet med kalkstensfri cementproduktion så innebär den ytterligare integrationen av cementproduktion till kolkraftverket med kalciumlooping en mindre reduktion av termiskeffektivitet (från 37.5% till 37.3%).

Kurzfassung

Kohlenstoffdioxidabscheidung und –speicherung (CCS) kann bei dem Versuch den Klimawandel zu stoppen eine entscheidende Schlüsselfunktion spielen. Unter den Technologien, die heute für die CO_2-Abscheidung verfügbar sind, nutzt Calcium Looping die Reaktion von Kalk (CaO) und CO_2 zu Kalkstein ($CaCO_3$) bei mittlerem Temperaturniveau. Diese Reaktion kann bei einem höheren Temperaturniveau umgekehrt werden, um das reine CO_2 freizusetzen. Dieser Prozess beruht auf gut bekannten Technologien, aber diese Anwendung zur CO_2-Abscheidung wurde erst kürzlich vorgeschlagen und ist daher weniger verbreitet als andere CO_2-Abscheidungstechologien, die auf chemischer Absorptions beruhen und zum Beispiel Amine oder Ammoniak als Sorbens nutzen. Der Grund hierfür ist, dass Brennstoff wegen der hohen Temperaturen benötig wird. Daher kann die CO_2-Abscheidung mittels Calcium Looping als wettbewerbsfähige Lösung angenommen werden, sofern Brennstoff in großen Mengen vorhanden ist, zum Beispiel in Kohlekraftwerken. Zusätzlich bietet sich eine interessante Option in der Tatsache, dass eine gewisse Menge des verbrauchten Sorptionsmittels (Kalk) aus dem Calcium Looping Prozess anfällt und dieser Kalk für andere Zwecke weiter verwendet werden kann. Dieser Fall ist in der Zementindustrie gegeben, wo der Kalk des Calcium Looping Prozesses den Bedarf an frischem Kalkstein sowie den Energieverbrauch für das Brennen des Kalksteins zu Kalk reduzieren kann. Das Ziel der Arbeit ist es, die Möglichkeiten zur Prozessintegration von CO_2-Abscheidung mittels der Calcium Looping Technologie hauptsächlich aus der thermodynamischen Sicht zur optimalen Wärmerückgewinnung für die beiden relevantesten Anwendungsfälle – Kohlekraftwerk und Zementfabrik – zu untersuchen. Die Pinch-Analyse wird angewendet, um die Konsequenzen der Integration des Calcium Looping Prozesses auf die Prozesswärme und Energiebilanz unter idealen Wärmerückgewinnungskonditionen abzuschätzen. Hierfür wird ein Prozessmodell erstellt und Simulationen werden durchgeführt, sodass Informationen über Temperatur und Wärmelast in den verschiedenen Systemteilen gewonnen werden.

Die Arbeit ist in zwei Teile aufgeteilt: die Integration von Calcium Looping mit einem modernen Kohlekraftwerk und die Integration von Calcium Looping mit einer Kombination aus Kraftwerk und Zementfabrik. Die Prozesssimulation ist wiederum aufgeteilt in die Simulation des Calcium Looping Prozesses, die Simulation eines Kohlekraftwerks mit Calcium Looping für die CO_2-Abtrennung und die Simulation einer Kombination aus Kohlekraftwerk und Zementfabrik mit einem gemeinsamen Calcium Looping Prozess. Es werden drei verschiedene Konfigurationen für die Integration mit einem Kohlekraftwerk untersucht: zwei Fälle unter der Annahme von seperatem Wasser-Dampf-Kreislauf für die Wärmerückgewinnung im Calcium Looping Prozess (jeweils unterschiedliche Komplexität) und ein Fall mit gemeinsamen Wasser-Dampf-Kreislauf, wo sowohl die überschüssige Wärme vom Kraftwerk als auch die des Calcium Looping Prozesses zurückgewonnen und in denselben Kreislauf übertragen werden. Um den Effekt der Prozessintegration von Calcium Looping bewerten zu können wird der thermische Wirkungsgradverlust des Kaftwerks als Indikator verwendet. Zum Vergleich wird ein Oxy-fuel Kraftwerk mit CO_2-Abscheidung durch Kondensation des Wasserdampfes in die Betrachtungen aufgenommen. Der Fall, in dem Calcium Looping mit dem Kraftwerk gemeinsam in einen Wasser-Dampf-Kreislauf integriert wird, erzielt die besten Ergebnisse in Bezug auf den elektrischen Wirkungsgrad mit einem Wirkungsgradverlust von 5,3%-Punkten im Vergleich zum Bezugskraftwerk ohne Calcium Looping (42,8% zu 37,5%). Die Analyse der Integration zwischen Kohlekraftwerk, Zementfabrik und Calcium Looping ist auf zwei Arten durchgeführt worden: zuerst eine Zementfabrik mit konstanter Produktion entsprechend der Referenzfabrik und dann eine Kalkstein-freie Zementfabrik, bei der die Produktion so angepasst wurde, dass nur der abgeführte Kalk aus dem Calcium Looping genutzt wird. Zur Bewertung werden verschiedene Parameter herangezogen, wie der thermische Wirkungsgradverlust in Bezug auf das Referenzkaftwerk, der spezifische Kohleverbrauch für die Zementherstellung und die Verminderung der spezifischen THG-Emissionen der Kombination aus Zementfabrik und Kraftwerk. Im Fall der Kalkstein-freien Zementfabrik führt die Integration mit Kraftwerk und Calcium Looping lediglich zu einem geringfügigen Wirkungsgradverlust (37,5% zu 37,3%).

Contents

Abbreviations

CaL/CaLooping	Calcium Looping
CCS	Carbon Capture and Storage
CFB	Circulating Fluidized Bed
E_{co2}	CO_2 capture efficiency
ESP	Electrostatic precipitator
F_{CaO}	Molar flow of CaO
F_{CO2}	Molar flow of CO_2
HP	High pressure turbine
IP0/1/2	Intermediate pressure turbine
J	Joule, measure of work (energy)
kW	Kilowatt, measure of effect
kWh	Kilowatt hour, measure of energy
LVH	Lower heating value
LP	Low pressure turbine
MEA	Monoethanolamine
$\dot{m}$	Mass flow
NJV	Nordjyllandsværket, power plant in northern Denmark
p	Pressure
P	Power
s	Entropy
T	Temperature
T_{CW}	Temperature of cooling water
VHP	Very high pressure turbine
W_{el}	Specific electricity output
W_{th}	Thermal output
X_{carb}	Fraction of $CaCO_3$ to CaO after the carbonator

ΔH	Enthalpy of formation
ΔT_{min}	Minimum temperature difference
η_{el}	Electrical efficiency

1 Introduction

Since the start of industrialisation there has been a marked increase in concentration of the greenhouse gases (mainly CO_2, CH_4 and NO_x) in the atmosphere compared to pre-industrial levels (IPCC, 2013). It is generally accepted that human activities are the source for the rise in atmospheric concentration of greenhouse gases, but the long term effects of the increase are not entirely known. There are however certain indicators of change in the climate that are possible to monitor, such as: surface temperature, water vapour in the atmosphere, sea level, ice coverage on land and sea, glaciers and abnormal weather occurrences. In all of these areas the scientific community have observed changes which are considered as detrimental and if left unchecked may lead to serious consequences for the whole planet (IPCC, 2013).

There are several possible strategies to reduce emissions to the atmosphere. One approach is to capture the carbon dioxide and store it away in a suitable storage place, such as underground geological formations. This technique is popularly called Carbon Capture and Storage (CCS) and one such method of carbon capture, namely calcium looping, will be the main topic of this thesis.

As over 80 % of the world primary energy supply comes from fossil sources (IEA, 2013), the main advantage with CCS is that it can allow the continued use of fossil fuels while at the same time minimizing the emissions to the atmosphere and thus reducing the need for urgent replacement of existing plants with for new renewable alternatives, or other strategies, to meet emission targets. Another aspect is that CCS may be a valuable to ensure energy security of a country while at the same time limiting emissions. For example Poland is a country with large coal reserves and a large political desire to remain independent from other countries when it comes to energy supply (Polish Ministry of Economy, 2009).

While there are variations between different methods of carrying out CCS, the basic principle is often the same: separate the $CO_{2,}$ compress it and transport it to storage and finally store it in a suitable location. While the research on capture technologies was already very successful and those technologies are established the main limitation in the CCS technology is the storage.

This thesis focuses on the capture and specifically on a technology of capture called calcium looping, or Ca-looping. Calcium looping as a technology for carbon capture using twin fluidized bed reactors was initially proposed by Shimizu et al. (1999). Limestone sorbent (CaO) is used to capture carbon dioxide through chemical reaction by formation of calcium carbonate ($CaCO_3$) in one reactor (absorber or carbonator) and then transporting the $CaCO_3$ over to a second reactor (regenerator or calciner) where the a reversed reaction occurs for recovering the limestone and releasing CO_2. The separated CO_2 is then compressed and stored.

2 Objective

In this thesis the *calcium looping* technology for capture of CO_2 and storage will be investigated from a thermodynamic point of view by means of process simulation and analysis of heat integration opportunities. The aim is to identify the thermodynamic characteristics of the process and to find optimal thermal integration options in relevant processes such as coal power plants, cement plants as well as a combination of the two. The focus is firstly put on estimating the effect that the carbon dioxide sequestration has on the electrical efficiency of a state of the art coal power plant. Secondly the application of the calcium looping technology to a combination of cement plant and coal power plant will be investigated.

3 Scope

The work starts with establishing a simple thermodynamic model of the calcium looping technology. This model is used in order to assess the consequences in terms of primary energy and process complexity of implementing such technology in relevant energy intensive processes based on fossil fuel combustion. The emphasis is on the thermal behaviour of the two reactors used for calcium looping and the range of values of operating parameters (temperatures, pressures, flow rates, etc.).

Post-combustion applications of the calcium looping are of most interest due to easier implementation in existing combustion plants. For time management reasons the thesis does not handle pre-combustion application although an overview of it is given in the introduction.

A preliminary literature survey indicates the coal power plants and cement plants as the most relevant cases of applications for the calcium looping technology. In these processes a huge amount of CO_2 is released and the by-product of the calcium looping can potentially be used in both plants which can offer further advantages. In the cement plant in particular, an additional process integration opportunity between the calcium looping and the cement production process consists in replacing some of the raw limestone in the cement plant with the purged lime from the calcium looping process. This is interesting as a large amount of CO_2 is normally emitted during the calcination of limestone to provide fresh lime to the cement production.

The investigation of the effect of the calcium looping technology on the performance of a coal power plant and cement plant is conducted using process integration tools such as Pinch Analysis. The thermal characteristics (temperatures and heat loads of main process steps) of the calcium looping process as well as of a state of the art coal power plant are identified by process simulation based on data collected from literature. Pinch Analysis is used to estimate the integration of a steam cycle (or more than one) with the conventional coal combustion and with the calcium looping process. This allows estimating possible penalty in electrical efficiency as well as proposing interesting integration options (i.e. process configurations) to reduce such penalty.

4 Carbon Capture and Storage

Carbon capture and storage is a technology for separation, transportation and storage of CO_2 from a fuel conversion process. The CCS technologies differ by point of CO_2 capture and normally classified into three categories: into post-combustion, pre-combustion and oxy-fuel. In this chapter an overview of the technology chain of the different capturing technologies is given.

4.1 Post-combustion

In post-combustion the CO_2 is captured after the fuel has been burned.

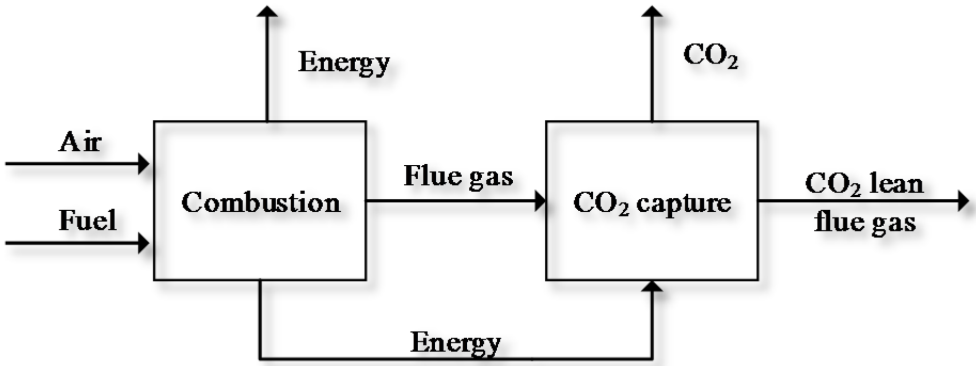


Figure 1: Overview of post-combustion process, adapted from (Global CCS Institute, 2014; Hektor, 2008)

As shown in Figure 1, in the post-combustion process the fuel is burned with air as in a process without CCS technology. In the flue gas cleaning train a CO_2 capturing unit is integrated. In this capturing unit the flue gas stream is separated in two different streams, a CO_2 lean flue gas stream and a CO_2 stream (Global CCS Institute, 2014).

In the separation unit the CO_2 reacts with a sorbent or solvent (depending on chosen technology for separation) and is lead away to be treated in another stage to release the CO_2 and regenerate the sorbent (Global CCS Institute, 2014). Examples of solvents are monoethanolamine (MEA) as used in CO_2 scrubbers (Global CCS Institute, 2014) and ammonia as used in the chilled ammonia process (Hektor, 2008). In the calcium looping process, the sorbent is lime (CaO) (Shimizu et al., 1999).

The main advantage of the application of CCS as a post-combustion technology is that existing power plants can be retrofitted with this technology without difficult changes in the existing plant as it is applied to the flue gas train.

4.2 Pre-Combustion

In pre-combustion processes the CO_2 is captured after a gasification or reforming unit (where syngas is produced) and before the syngas (or hydrogen) is burned (Figure 2).

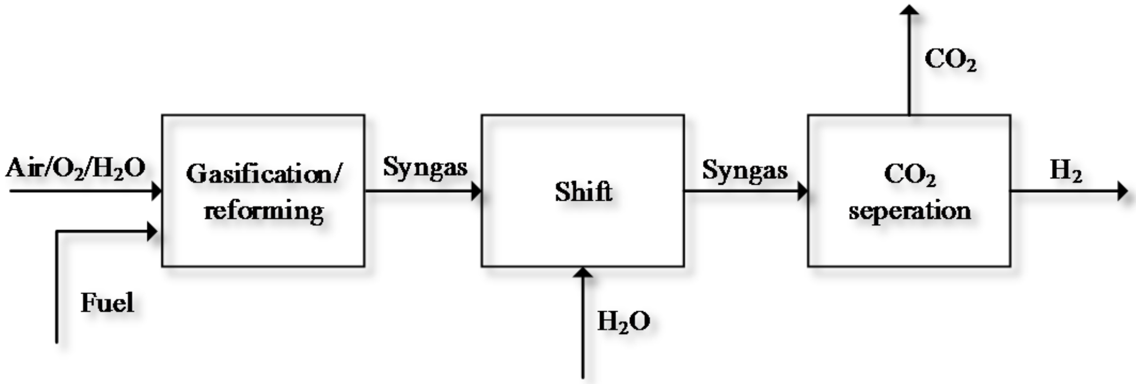


Figure 2: Overview of pre-combustion process, adapted from (Global CCS Institute, 2014; Hektor, 2008)

The first step is to create a syngas from the fuel. This step is carried out via gasification or reforming dependent on the fuel that is used. The syngas is a mixture of CO, H_2, CO_2 and often other hydrocarbons. In order to obtain a final gas rich in H_2, which produces water when burnt, the quantity of H_2 is increased by a water gas shift reaction, where CO is shifted into CO_2 in presence of water. The carbon is in this way removed is form of CO_2 (Hektor, 2008).

When pure H_2 stream is produced this can be lead to a gas turbine, where energy is generated and the CO_2 free exhaust gas released (Global CCS Institute, 2014). Other utilizations of syngas or H_2 are also possible.

In the CO_2 separation unit basically the same technologies and sorbents can be used as in the post-combustion process. Calcium looping is therefore also an interesting option in this case (Blamey et al., 2010).

4.3 Oxy-fuel combustion

In oxy-fuel processes the CO_2 is captured during combustion as pure oxygen is used as oxidant and the product gas consists mainly of CO_2 and water which can be easily separated. Flue gases can also be recirculated in order to limit the high temperatures of combustion in presence of pure oxygen. A schematic overview is given in Figure 3.

Air separation unit is necessary for supplying pure oxygen. The N_2 is released back to the surroundings (unless used for ammonia synthesis), whereas the O_2 is used for the fuel combustion. Here the main reaction is between carbon and oxygen; therefore the flue gas consists mainly of CO_2, but free of nitrogen. As the other big component of the flue gas is water, a condenser is used where the water is separated from the CO_2 by cooling down the flue gas stream (Global CCS Institute, 2014).

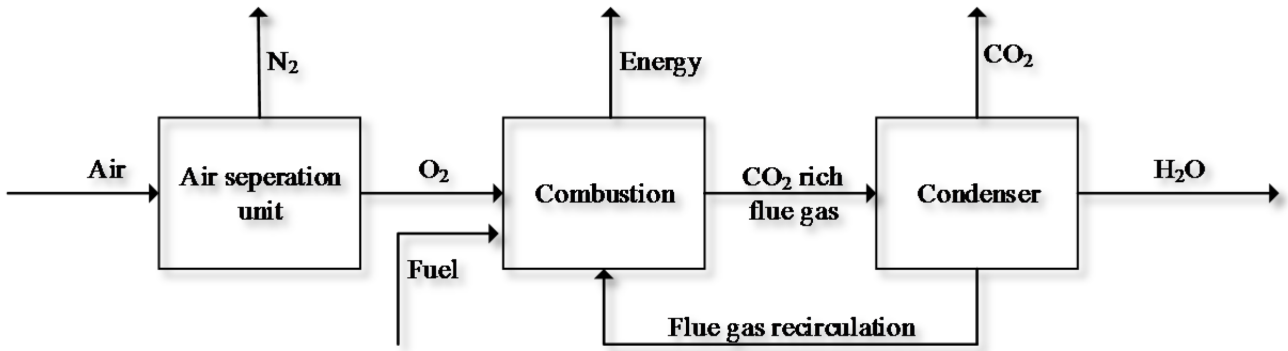


Figure 3: Overview of oxy-fuel combustion process, adapted from (Global CCS Institute, 2014; Hektor, 2008)

The main disadvantage of this carbon capture method is the highly expensive air separation unit and on the particular combustion conditions, but on the other hand the advantage is a much simplified CO_2 separation stage (Global CCS Institute, 2014).

4.4 Transportation and Storage

After capturing the CO_2 needs to be compressed to be transported from the emission point to the storage point. The transportation will manly take place like for oil and gas via pipelines. A network of pipelines will transport the compressed CO_2 from the industry to the storage point (Global CCS Institute, 2012). If pipelines aren't sufficient, tankers can be used (Hektor, 2008).

The CO_2 then can be stored in geological formations, ocean storage or mineralization. The most common method to store it is using geological formations such as depleted oil or gas reservoirs, deep saline aquifers or un-mineable coal seams. Important is that the risk for leakage is very low and the possibilities for monitoring good (Pickup, 2013).

4.5 Carbon Capture and Reuse

Another possibility is the Carbon Capture and Reuse. This option is based on production of methane using Sabatier's reaction. The captured CO_2 can be used to produce methanol, acetic acid, electricity and hydrogen (Ng et al., 2013).

5 Calcium looping

Calcium looping is a technology for CO_2 capture that can either be used in pre-combustion or post-combustion (Blamey et al., 2010). This technology uses double circulating fluidized bed (CFB) reactors filled with a sorbent, e.g. limestone. In the first CFB reactor, the carbonator, the CO_2 is captured by chemical reaction of CO_2 and the sorbent and released in the second CFB reactor, the regenerator, by an endothermic reaction (Blamey et al., 2010). One big advantage of this technology is that the reactors and other parts of the rig are already commercially established in large scale (Alonso et al., 2009). In this chapter a brief literature survey will be given and the main focus will be on post-combustion applications.

5.1 Process description

The initial concept of calcium looping was proposed by Shimizu et al. (1999) using calcium oxide to capture CO_2. As this concept was very promising, in the following years several research and developing studies in micro scale were carried out, as well as process modelling and simulation and first economic studies. The results of those studies lead to bench scale studies between 2006 and 2009 to prove the feasibility. Therefore small rigs in a scale up to 100 kW_{th} were built in different countries. In the following years a scale up to pilot plants ($100kW_{th}$ – $2MW_{th}$) was done to demonstrate the process under realistic process conditions. As these pilot plants brought great results the data is used for future development of the technology (Dieter et al., 2014).

Besides modelling, simulations and demonstrations also a great effort was put in studies about the sorbents, their development and activation (Dieter et al., 2014).

Post-combustion calcium looping can be used in different combustion processes and will be integrated in the flue gas cleaning train. The main components of this technology, shown in Figure 4, are the two CFB reactors, the carbonator and the regenerator. Into the bed of the regenerator, also called calciner, a sorbent is injected. Usually limestone is used, therefore in the following description limestone is written for non-calcined sorbent and lime respectively for calcined sorbent. At a temperature around 850°C to 950°C the limestone is calcined. The heat supply can result from different applications – heat transfer, combustion or electric heating. After calcination the lime is carried out of the reactor by the fluidizing gas stream and separated from the gas in a cyclone; thereafter it is lead to the carbonator. The carbonator is fluidized by the flue gas from the initial combustion. Here the limestone is carbonated at a temperature of 650 to 700°C and in the cyclone the stream gets separated into a CO_2 lean flue gas stream and a stream of solids going to the calciner for regeneration (Alonso et al., 2009).

The limestone releases the CO_2 at high temperature in the regenerator again. In the cyclone a CO_2 stream is separated from the solids and the CO_2 can be compressed and stored.

Due to different mechanisms, such as for example sintering and calcium sulphate formation, sorbent eventually becomes deactivated and must be purged from the system. To compensate for this loss of the deactivated sorbent, fresh limestone is continuously injected in the regenerator in the same amount as the spent sorbent is released (Alonso et al., 2009).

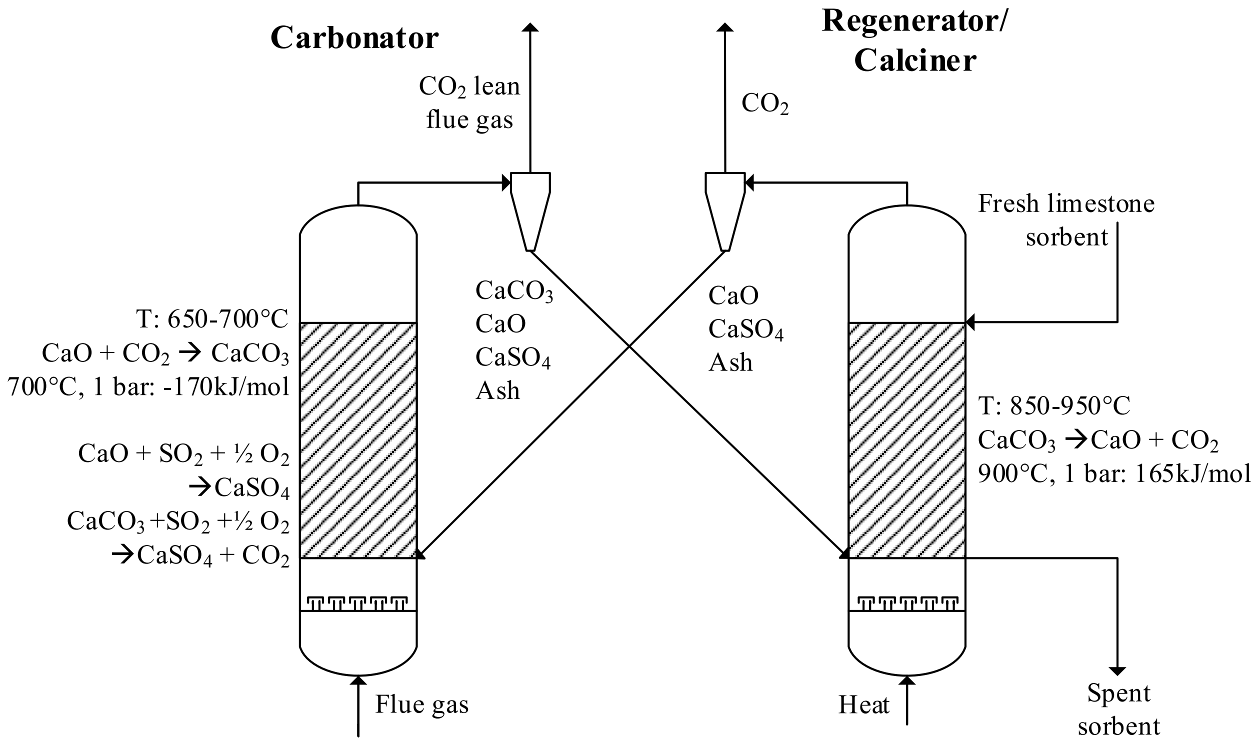


Figure 4: Calcium looping process, adapted from (Blamey, 2010; Dean, 2011)

Calciner/Regenerator

In the calciner the reaction of limestone being calcined and releasing the CO_2 is shown below.

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \Delta H = 165 \text{ kJ/mol} \qquad (1)$$

Reaction (1) is endothermic which is why heat has to be supplied in the calciner.
This calcination is carried out at high temperature levels. Considering sintering and competing reactions such as $CaSO_4$ formation, and the deactivation of sorbent caused by these factors, the optimum temperature is 900°C at maximum (Dean, 2011).

The typical duration of a complete calcination process is 0 – 15 minutes. The longer the sorbent is exposed to the high temperature the stronger the impact of deactivation (such as sintering) is. Therefore the calcination should be kept as short as possible.

Researches have shown that a higher efficiency in calcination can be achieved in the presence of water vapour. With already a water content of 20% a significantly higher calcination rate can be reached (Blamey et al., 2010).

In Figure 4 above it can be seen that heat is provided in the regenerator to reach the high temperature that is needed to regenerate the sorbent and release the CO_2. In the original proposal by Shimizu et al. (1999) this heat was provided by in situ oxy-fuel combustion in the regenerator. This will require an air separation unit to be installed and additional (in addition to the main fuel provided in the power plant) fuel will have to be provided to the regenerator.

5.1.1 Carbonator

CaO is transported to the carbonator where the exothermic reverse reaction (2) occurs:

$$CaO + CO_2 \rightarrow CaCO_3 \qquad \Delta H = -170 \text{ kJ/mol} \qquad (2)$$

Besides this reaction the CaO also reacts with the SO_2 in the flue gas. This reaction and the calcination reaction limit the temperature of the carbonator to maximum 700°C. Above this temperature the reaction rate of CaO with sulphur rises and the $CaCO_3$ releases the CO_2 again (Dean, 2011).

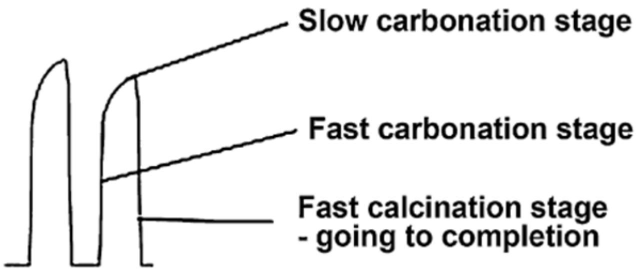


Figure 5 Carbonation/Calcination mechanics, adapted from Dean et al. (2011)

The carbonation process can be divided into two stages: the fast carbonation stage and the slow carbonation stage. In the fast carbonation stage the CO2 is bond on the surface of the CaO whereas in the slow carbonation stage diffusion takes place and CO2 is also bond in the CaO particle.

The duration of complete carbonation process is there for longer than the duration of a calcination process. According to the literature the duration for carbonation is above 30 minutes.

These facts and the loss of capacity (see chapter 5.2.1) lead to a higher demand of sorbent than a stoichiometric reaction requires (Blamey et al., 2010).

5.1.2 Alternative set-up

To avoid using an air-separation unit alternate set-ups of the calcium looping process are possible, such as the three reactor set-up that was investigated in the work of Martínez et al. (2011). This set-up used a third fluidized bed reactor where heat required for the process is supplied by standard combustion and transferred to the calciner using a high temperature solids stream. The flue gases from the combustion in the third reactor are directed to the carbonator.

5.1.3 Deactivation of sorbent

The mass flow of solids stream consists of the sorbent CaO, the carbonated sorbent $CaCO_3$ and deactivated sorbent such as $CaSO_4$ and ash. In the following part the basic principles of deactivating the sorbent are explained.

During the combustion of fuel with a sulphur content SO_2 is formed which leads to a competitive reaction with CaO. For the reaction of CaO and sulphur oxide two different possibilities exists:

$CaO + SO_2 + ½ O_2 \rightarrow CaSO_4$ $\Delta H = -502\ kJ/mol$ (3)

$CaCO_3 + SO_2 + ½ O_2 \rightarrow CaSO_4 + CO_2$ $\Delta H = -324\ kJ/mol$ (4)

The critical aspect about these reactions is that they dominate the formation of $CaCO_3$ due to the specific value differences in ΔH. The influence depends on the sulphur content in the flue gas. The reaction can also occur in the regenerator when the heat supply is achieved by oxy-fuel combustion (Blamey et al., 2010).

The critical aspects of $CaSO_4$ are that it has a higher molar weight and higher volume, which means that the pores close faster and the loss of surface area is bigger while at the same time the regeneration of $CaSO_4$ is only possible at very high temperature and therefore impractical (Dean, 2011). This, as the deactivation of the sorbent due to sintering, increases with raising temperature and the efficiency penalty induced to reach the needed temperature levels also increases (see more in chapters: 5.2.1 and 5.4). The $CaSO_4$ circulates as in inert component in the solids stream.

Another inert circulating component is the ash from combustion processes. Both components are only relevant for the mass flow.

In addition to the formation of $CaSO_4$ losses in the capacity of the sorbent occur due to high temperature. It comes to sintering and the surface area of the particles is reduced. Therefore less CO_2 can be captured per cycle (Dean, 2011).

All these losses in the sorbent make it necessary to inject fresh limestone and reject the spent sorbent (Alonso et al., 2009).

5.2 Sorbents

In the first suggestion of the calcium looping process as made by Shimizu et al (1999) the sorbent that was used was limestone. Limestone has continued to be the base sorbent for the calcium looping process and most research has concentrated on the properties of it, but there have been some research into alternative sorbents as well (Coppola et al., 2013). The main parameters that measure differences between the sorbents are their capture capacity, resistance to sintering and attrition (which affects sorbent deactivation rate) and the cost of the sorbent. A rough comparison of the main types of sorbents is given below:

<u>Limestone:</u> a natural sorbent, whose large advantage is that it comes at a low cost owning to the fact that it is in essence grinded rock. Allows for a high initial capture capacity of CO_2, but suffers from a clear degradation in this capacity over a number of cycles in the calcium looping (Blamey, 2010).

<u>Dolomite:</u> a natural mineral with a cost slightly above that of limestone. Dolomite is found to have a better long term carbon capture capacity and is characterized by being less susceptible to sintering than limestone. But as dolomite has a lower initial capture capacity than limestone more dolomite must be added to the system compared to limestone and dolomite is also a more brittle sorbent than limestone meaning that attrition and fragmentation will be much more extensive compared to limestone (Coppola et al., 2013).

Altered sorbents: In attempt to compensate for the shortcomings of the natural sorbents research has been carried out to find different enhanced sorbents as increase performance and reduce deactivation in the calcium looping process. Main methods of enhancement that have been investigated consist of either doping natural limestone with for example organic salt, producing new synthetic sorbents from a limestone base or exposing the sorbent to thermal pre-treatment. Different studies have been able to show improvement in sorbent properties, but all methods share the drawback of adding more complexity to the system which may prove to be negative from an economic perspective (Dean, 2011).

5.2.1 Sintering

When solid particles are heated up to high temperatures, but are still under their melting point, they will start to merge. For a porous material, such as the sorbents for calcium looping, this means that the small pores in the material will shrink and close as all the grains that initially form the sorbent will fuse together to form larger grains. This effect, which is more noticeable at high temperatures and long durations of reaction, is called sintering and it has the end result of a drop in reactivity for the sorbent as the surface area and porosity of the particle will become smaller than before (Borgwardt, 1989).

If the temperature becomes too high (above 900°C for CaO) sintering occurs at an elevated pace, meaning that the makeup flow of sorbent will increase accordingly and that it will be in the calciner that the sintering predominantly will occur. The presence of H_2O though, in the form of steam, in the reactor will affect the breaking point for the increased sintering rate making it occur at lower temperatures than it would have otherwise (Blamey et al., 2010).

With several cycles of carbonation and calcination the sintering will thus make the sorbent less and less able to capture CO_2 which, along with eventual $CaSO_4$ formation, is the main reason for sorbent deactivation and the subsequent need for a makeup flow of fresh sorbent. In Figure 6 the change in carrying capacity of CaO is shown for a period of 50 cycles of looping in a calcium looping process.

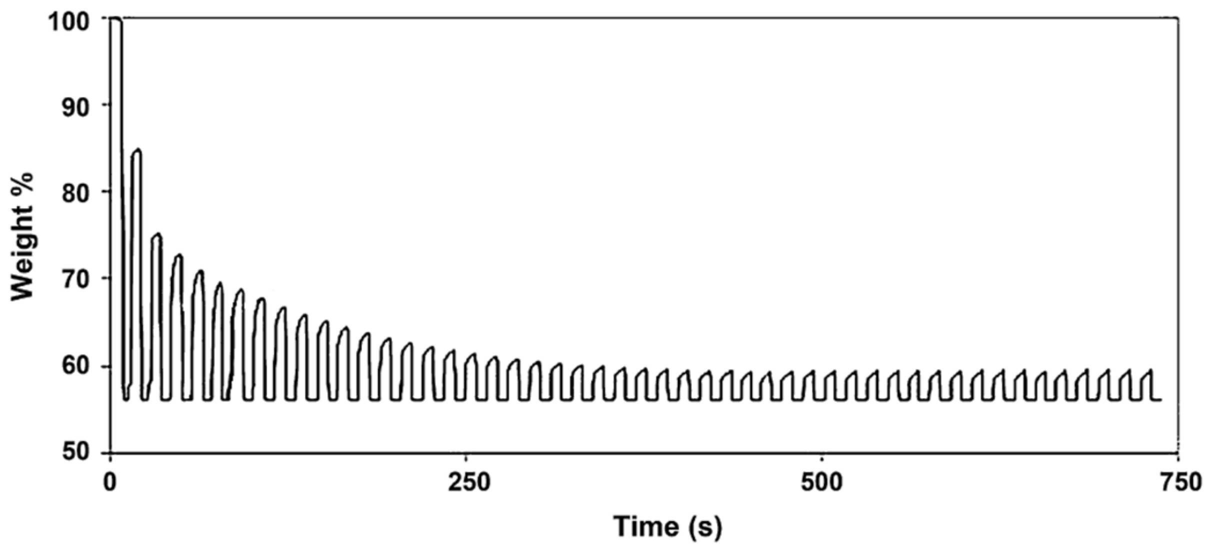


Figure 6: Carrying capacity of CaO shown as change in mass against time, adapted from Dean et al. (2011)

5.2.2 Attrition

Another process that leads to loss of sorbent is attrition. While not the foremost cause of sorbent loss, attrition is still one of the most relevant processes for loss of sorbent and is especially prominent with more brittle sorbents such as for example dolomite (Coppola et al., 2013).

Attrition occurs due to mechanical forces acting upon the particles in the fluidized bed, causing them to break into smaller and smaller parts until they are typically less than 0.1 mm in size (Blamey, 2010) at which point they are no longer possible separate and cycle back in the cyclone. Experiments by Lu et al. (2008) showed that the largest amount of attrition occur in the calciner, which they argued was most likely due to the brittleness of the sorbent after the adsorbed CO_2 is released from the surface and pores of the sorbent, in addition to effects of sintering etc. in the high temperature environment.

5.2.3 Possibilities for use of deactivated sorbent

One possibility to use deactivated sorbent that mainly consists of lime is to replace the lime used in a cement plant. In a cement plant a huge part of the raw material input consists of limestone that needs to be calcined for the further process. This limestone can be partly or completely replaced by purge from a calcium looping process that does not need to be calcined anymore. This symbiosis of power plant, calcium looping and cement plant is further described in chapter 7.2.4.

Another possible use of the deactivated sorbent is to recycle the purge flow to the main combustion reactor of the system to capture sulphur oxide. By capturing the sulphur oxide directly in the combustion unit with the deactivated sorbent, the problems with $CaSO_4$ formation in the calcium looping process are minimized without affecting the performance of the capture or adding anything extra to the system (Cordero et al., 2014). Experiments done by Cordero et al. (2014) also indicate that using deactivated sorbent would result in an efficiency of SO_2 capture that is more than two times as high as for using the fresh limestone directly without first being used in the calcium looping process.

5.3 Capture efficiency

While it is theoretically possible to reach a maximum capture efficiency of 100% using calcium looping technology (Abanades, 2002) it may not be the most efficient solution when looking from economic or energy efficiency point of view. As has been mentioned earlier, the capture capacity of the sorbent is not used fully and the capacity will decrease over time due to sorbent deactivation mechanics, which leads to the need for injecting fresh sorbent to keep up the capture efficiency of the system.

Abanades (2002) showed that the relation between capture efficiency and amount of sorbent is that the more sorbent that is circulated in the system the better the capture efficiency will be, but warned that too high amounts of sorbent circulation could lead to excessive heat demand for the regeneration of the sorbent in the calciner. To sustain high capture efficiency while having less sorbent circulating in the system would require a higher rate of injection of

fresh sorbent, but this is also something that is desirable to keep at reasonable and lower levels (Abanades, 2002), due to for example economic reasons.
Hawthorne et al. (2009) also takes the circulation of sorbent into account and defined the CO_2 capture efficiency, E_{CO2}, through the following equation:

$$E_{CO_2} = \frac{F_{CaO}}{F_{CO_2}} * X_{carb} \quad (5)$$

In equation (5) F_{CaO} and F_{CO2} are defined as the molar flows of CaO and CO_2 to the carbonator respectively. X_{carb} is the fraction of the CaO molecules in circulation that are reacting with CO_2 to form $CaCO_3$. X_{carb} will depend on the condition of the sorbent and will be higher with increased rates of make-up flow of sorbent, as the sorbent loses reactivity with each cycle, but Hawthorne et al. (2009) cite the typical fraction in the range of 5 – 15%. Sulphur content in the flue gas will affect the capture efficiency as the sorbent will react with the sulphur before the carbon dioxide (as described in chapter 5.1.3).

Experience from lab scale and pilot scale setups have shown that high capture efficiencies of over 90% are possible also in practice, which supports the main results of Abanades. These experiments have also shown carbonator operating temperature to have an important role for capture efficiency, with the optimum values said to be between 630 – 650°C (Dieter et al., 2014).

5.4 Energy demand

Calcium looping does not come free of charge, but carries with it an energy penalty as with other CCS technologies. This energy penalty occurs as extra energy is needed to run the new process in addition to compress the separated CO_2 for transportation and storage, energy which could have been used for other purposes. This may lead to higher environmental impacts, besides the decrease of global warming potential, as a direct result of the increase in energy demand (Corsten, 2013).

Post-combustion capture technologies, as is investigated in this thesis project, vary greatly in in energy penalty depending on variables such as for example chosen capture technology and configuration of the equipment. The thermal energy efficiency penalty when applying calcium looping to a coal power plant is reported to vary from around 4 – 18% depending on the previous stated variables (Corsten, 2013).

For calcium looping technology, Abanades et al. (2005) investigated the energy penalty for a process set up as suggested by Shimizu et al. in 1999 and found it to be around 7% if integrated with a coal power plant. The major part of the energy penalty was said to occur due to the compression of the separated CO_2 and the separation of O_2 for the combustion that provides energy for the calcination as per Shimizu et al.'s proposal. The energy penalty was seen to drop to around 6% if air separation was removed and calcination heat was provided by a dense solid heat carrier instead of flue gas from oxy-fuel combustion (Abanades, 2005). Other research performed indicates the possibility to get the efficiency penalty down as low as 4%, which indicates a positive outlook for the feasibility of the technology (Dieter et al, 2014).

5.5 Economic comparison

The viability of a technology is always dependent on its economic feasibility, thus it is important to investigate whether Calcium looping is competitive with other solutions for carbon capture or not. As the focus in this thesis will be on post-combustion carbon capture, calcium looping shall be compared to the other three most common methods for post combustion carbon capture; amine scrubbing with monoethanolamine (MEA), ammonia cleaning with chilled ammonia technology and oxy-fuel combustion.

As it is hard to estimate exact values, most of the costs of avoidance in Table 1 below are given in a range which is dependent on both outer factors such as fuel price, CO_2 tax, electricity costs etc. and in what applications the capture technologies are used. The investment costs are taken from various sources and presented as per kilowatt of output for the entire plant.

All costs are given in EUR (The costs are converted to EUR based on the average exchange rate from USD in the year when each estimate was made, for all values except avoidance cost for chilled ammonia and oxy-fuel processes). If more than one source is listed then the first source refers to avoidance costs and the second to investment costs.

Table 1: Economic comparison of carbon capture technologies

Technology	Cost of avoidance [EUR/t CO_2]	Investment cost [EUR/kW]	Source
Calcium looping	6 – 27	1140 – 1590	Abanades (2007)
MEA	26 – 65	650 – 1570	Blamey (2010) / IEA (2011)
Chilled ammonia	16 – 37	1210 – 2490	Hektor (2008) / IEA (2011)
Oxy-fuel	29 – 56	740 – 1920	Zero Emissions Platform (2011) / IEA (2011)

6 Pinch analysis

The method used to perform the process integration in this thesis work is based on pinch analysis, which is a technique for finding the minimum heating and cooling demand for a system and thereby minimizing external energy consumption. To this end all energy streams in the process are first divided into cold and hot streams (depending on if they take up or release heat, respectively) and these streams are matched against each other to maximize the internal heat exchange in the process. By finding the best heat transfer matches for the different internal heat streams, less energy is needed to be supplied and/or removed via external sources (such as through heaters and coolers) in that way achieving a more efficient energy use in the system.

Heat exchange is driven by the difference in temperature, and it follows that there has to exist a certain point when heat exchange is no longer feasible, as the driving force (the temperature difference) is too small and the heat exchanger area would have to be increased too much in order to compensate. A minimum temperature difference, $\Delta T_{min,}$ is introduced to show how close the streams can come when heat exchanging between them, without resulting in too large equipment. This temperature is chosen at user discretion, and will vary depending on what media is carrying/receiving heat, but can typically range from 10 – 20°C for water and steam uses.

When analysing the heat streams in a process using pinch analysis, the minimum temperature difference will coincide with the difference between the temperatures of the two composite curves (one for all cold stream and one for all hot streams) at the so-called pinch point. These composite curves are the graphical summations of heat streams in a system and the principle for their construction is shown below in Figure 7.

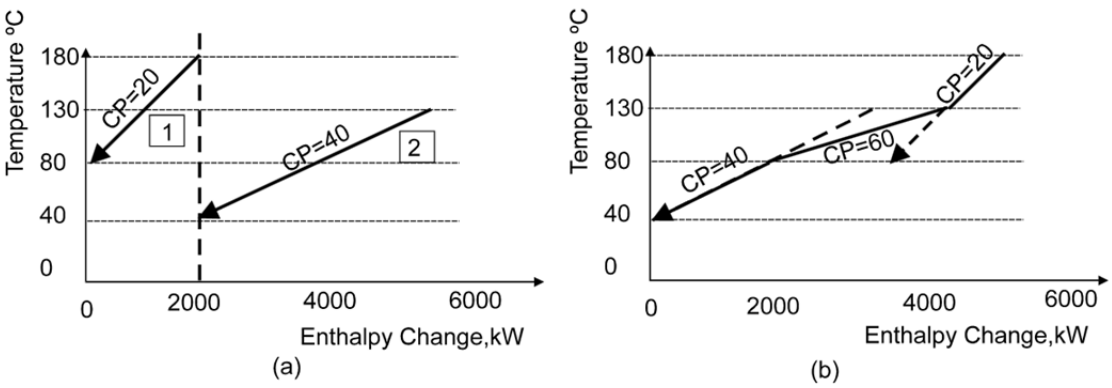


Figure 7: Construction of a (hot) composite curve, picture taken from Linnhoff March (1998)

The main tool for pinch analysis conducted in this thesis however, is the construction and further elaboration of the process grand composite curve, which serves as a graphical representation of the thermal characteristics of a process. In particular the grand composite curve represents the thermal cascade of a process, which is the net heat availability or demands along a relevant temperature scale. Such a curve allows for an immediate visualization of the process pinch point (where the curve touches the temperature axis) and of the hot utility and cold utility demand (the abscissa of the extremes of the curve).

The grand composite curve can also be seen as a composition of the hot composite curve and the cold composite curve of a process. The minimum temperature difference coincides with the difference between the temperatures of the two composite curves at the pinch point.

The construction of the grand composite curve is presented graphically in Figure 8 below.

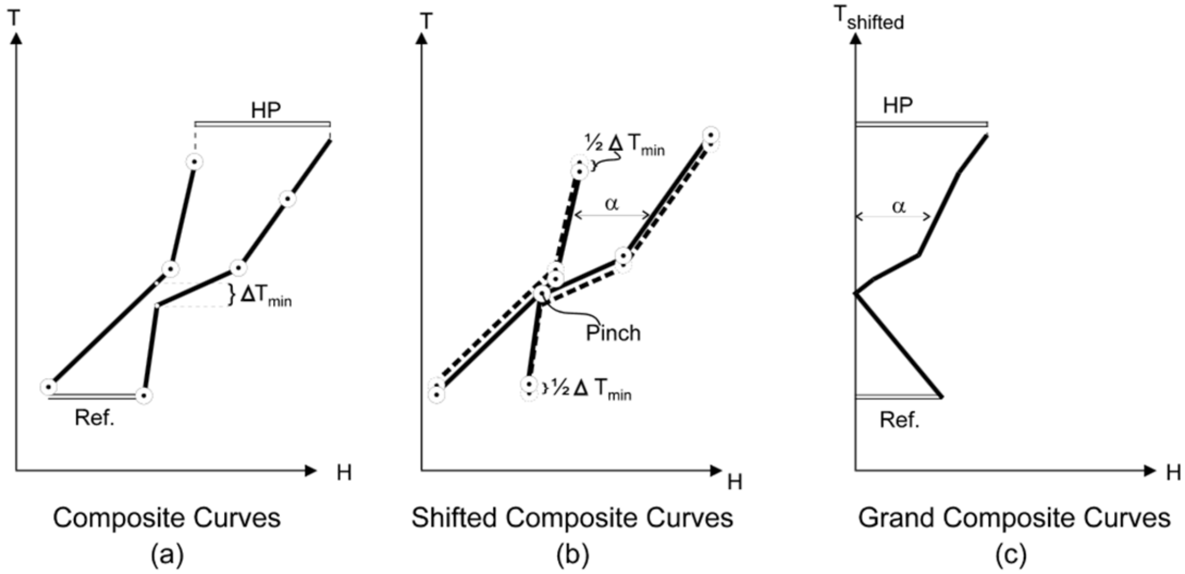


Figure 8: Construction of a grand composite curve, taken from Linnhoff March (1998)

For more detailed information on how pinch analysis works and how it was developed, see e.g. Linnhoff et al. (1982).

6.1 Foreground and background grand composite curve analysis

The grand composite curve of a process can also be used as a tool for investigating process integration possibility for the system. If the GCC for an existing system, as for example a coal power plant, is produced and held constant (i.e. the same coal flow and energy output and so on) another process can be integrated to the coal power plant by fitting a new GCC representing another process to fit the existing GCC for the coal power plant. The existing process is called the background process and the new process which is fitted to it is called the foreground process. The advantage here is to end up with a new process which is fitted to the background process as to utilize as much of the heat from it as possible.

As an example, for a coal power plant the combustion heat (radiative heat from the combustion chamber and the convective heat from the flue gases) serves as the constant background process. The foreground process, which is fitted to match the available combustion heat from the coal power plant, is in this case then the steam cycle. An example of how such a background/foreground GCC can look is shown in Figure 9 below.

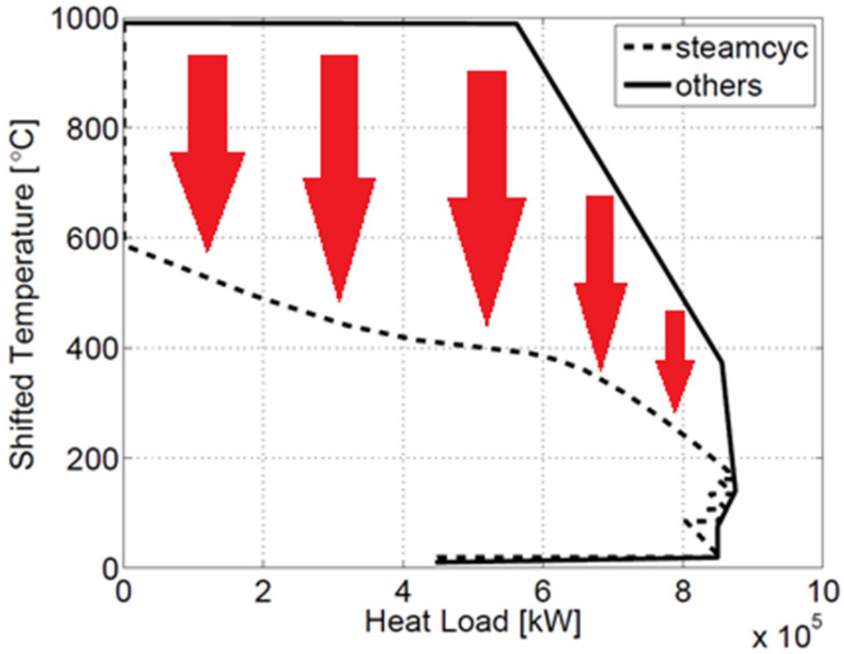


Figure 9: GCC of coal power plant with a 5 draw of steam cycle (direction of heat transfer shown with red arrows)

7 Methodology and work procedure

A literature survey is conducted to identify the state of art for calcium looping process, how it works in detail, where the current research is leading to and the potential of calcium looping applications. Typical values of important process parameters such as temperatures and pressure ranges, and capture efficiencies are collected from literature. This data is used for modelling and simulations of the calcium looping process which are carried out in ASPEN PLUS.

The model is then used to investigate the thermodynamic aspects of the CO_2 capture through calcium looping with specific attention to temperature and heat flows.

Once the model of the single calcium looping is established from removal of CO_2 from typical exhaust gases of coal combustion, the application of calcium looping under common conditions is investigated in more detail for selected industrial processes such as coal power plants and cement industry. Special attention is given to the effect that CO_2 capture has either on the electricity generation in power plants or in the primary energy demand of industrial processes. For this purpose data of a state of the art coal power plant and for a cement industry is gathered from literature. Due to intrinsic difference between the two applications, the work is conducted for each application separately. The coal power plant case is studied first.

Pinch Analysis tools are used for estimating the integration effects of the calcium looping technology for the two processes. This requires the definition of the temperature heat load profiles of the investigated process first (i.e. the coal combustion in coal power plants and the configuration of the steam turbine cycle, the main temperature and heat loads of a cement process). The temperature and heat load profile of the calcium looping, established form simulation results, are then used to investigate the effect of integrating this carbon capture to the basic processes. This corresponds to estimate the effect on power production for the coal power plant and the effect in terms of primary energy consumption for the cement industry.

Based on the reduction of CO_2 emission and on the energy consequences of implementing the calcium looping technology, an economic analysis could also be conducted in order to estimate the level of increased capital investment that can be accepted within interesting levels of profitability.

7.1 Presentation of study cases

In this thesis project the following cases regarding the feasibility of the integration of calcium looping technology in industrial processes are covered:

Basically the cases can be split into two main areas; coal power plant and cement plant. Within these main areas there are a couple of detailed configurations investigated, each configuration is represented by a study case. The study cases are listed and described in Table 2.

Table 2: Study cases

Short name	Main area	Description
1.0	Coal power plant	Base case coal power plant, simplified version of NJV
1.a	Coal power plant	2 steam cycles for the coal power plant and calcium looping process respectively. This case with a simple steam cycle for the calcium looping process.
1.b	Coal power plant	2 steam cycles as in 1.a, but with a more advanced steam cycle for the calcium looping unit utilizing reheat after the first turbine stage.
1.c	Coal power plant	Both the coal power plant and the calcium looping process integrated to 1 shared steam cycle.
1.d	Coal power plant	Reference coal power plant using oxy-fuel technology for the combustion.
2.0	Cement plant	Base case cement plant, taken from literature reference
2.a	Cement plant	Base case cement plant integrated in a shared calcium looping process with a power plant
2.b	Cement plant	Limestone free cement plant inspired by the base case cement plant.

The cement plant integration with a power plant and a calcium looping process is chosen due to the high amount of released CO_2 during the calcination of the limestone and the possibility of the reuse of the limestone used in the calcium looping process. This is described in detail in chapter 7.2.4.

7.2 Process modelling and simulation

In the following chapter the working procedure of the process modelling and simulation is described for all investigated processes in detail. In this chapter the basis for process integration (which is used to analyse the models) is also presented. The process modelling was done in four parts:

- Firstly, the calcium looping model was established using a base coal flow of 1 kg/s
- Secondly, a reference coal power plant was constructed based on the 'Nordjyllandsvaerket' power plant in northern Denmark
- Thirdly, an oxy-fuel burned version of this same coal power plant was modelled
- Lastly, a cement plant was modelled as, an extension of the initial model with calcium looping in a coal power plant, to investigate the possible benefits that could be gained there.

The modelling of all parts was carried out to gather the necessary information regarding mass and energy balance for each of the plants, to enable further investigation by means of process integration. The oxy-fuel fired coal power plant (using the same coal consumption as the reference coal power plant) is modelled as to put the calcium looping technology, as a method for carbon capture, into context directly with another competing technology. The choice of the oxy-fuel technology is based on the observation that the calcium looping technology in its original proposed configuration already uses oxy-fuel technology for the regeneration of limestone. The oxy-fuel model thus serves to answer the question of why not to use oxy-fuel combustion for the coal plant to achieve the CO_2 capture directly.

7.2.1 Calcium looping model

The calcium looping model, as shown in its entirety in Figure 13, was designed using Aspen Plus and consists of three major parts: the coal combustion section, the calcium looping section and the compression section.

The model was designed using case-study data and equations as presented in Dieter et al. (2014) and Vorrias et al. (2013), using a 1 kg/s coal flow to the combustion chamber as to model a representative base process for the calcium looping.

The overall capture efficiency was designed to be 90% under optimal conditions, i.e. none or low sulphur content in flue gas.

7.2.1.1 Coal combustion

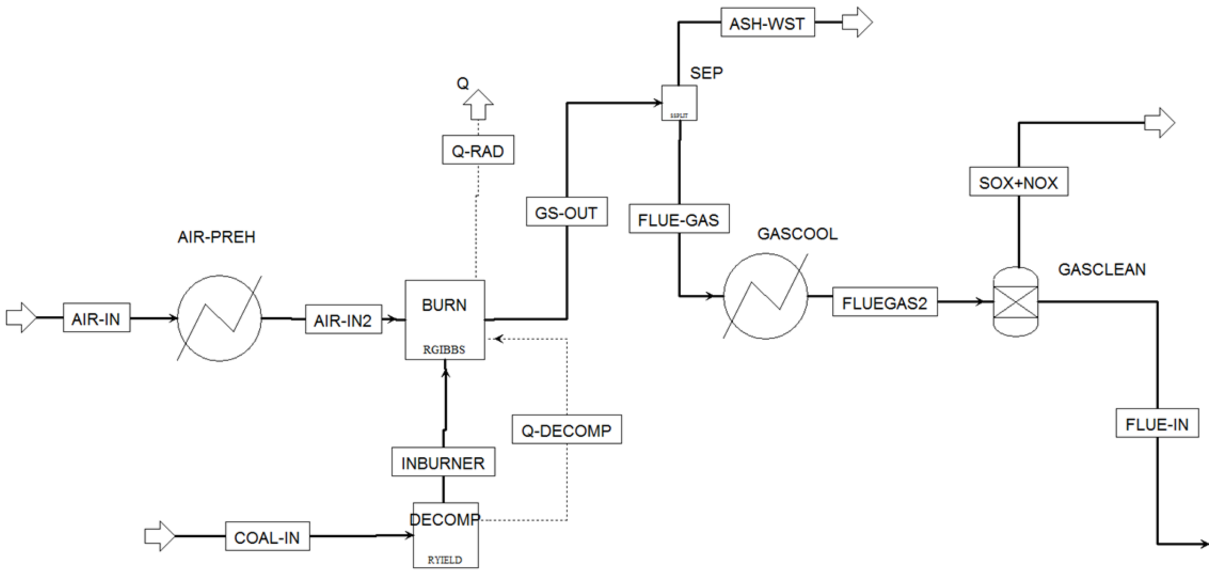


Figure 10: Coal combustion section

The coal combustion section was designed as to get the proper composition for the flue gas which enters the calcium looping section of the model, as to have as high accuracy as possible in the simulation. To that end, the coal that is used is the same coal as is used in the reference coal power plant, which is presented in the next chapter 7.2.2.

Aspen Plus does not have a built-in support for coal as a component, so it has to be added as a custom ‘non-conventional’ compound, which gives rise to the need to first enter the coal stream into a decomposer that breaks it down into it constituent parts. After the coal is broken down into components known to the program it can be transferred over to a reactor block where the combustion reactions with air can be calculated. The heat associated with the decomposition of the coal is transferred to the combustor block for correct modelling of heat production.

Before the flue gas is lead to the calcium looping section, ash, SO_x and NO_x (which are formed as a result of the combustion modelling) are separated from the gas with separator blocks using the reported gas cleaning efficiencies from the reference plant to determine pollutant content in the flue gas entering the carbonator.

7.2.1.2 Calcium looping

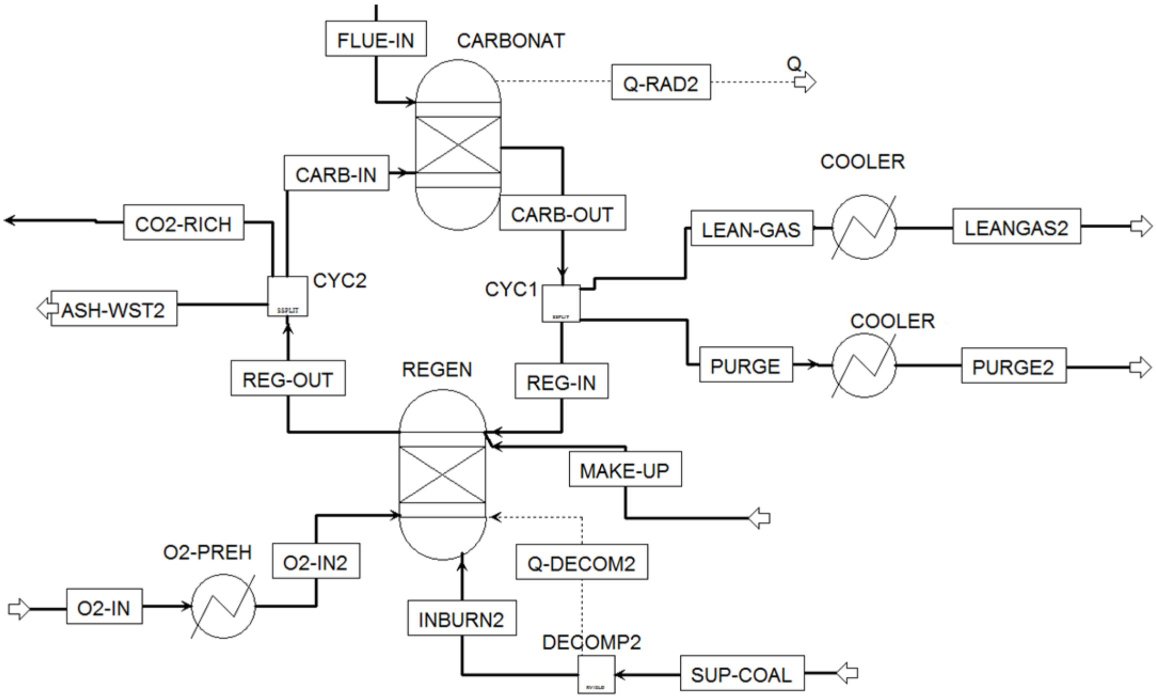


Figure 11: Calcium looping section

The calcium looping section was set-up with the carbonator in the top and the regenerator below, with extractions of lean gas and purged material on the right and extractions of CO_2 rich gas and ash from regeneration to the left. The simulation of coal combustion in the regenerator works similar as in the coal combustion section with a decomposition unit, but takes place with additional materials present and pure O_2 instead of air.

Based on Dieter et al. (2014) and Vorrias et al. (2013) the ratio between circulating sorbent and CO_2 in the calcium looping cycle was chosen to be 7 with a make-up ratio of 0.1 times CO_2 content in flue gas. The carbonator temperature is assumed to be at 650°C and the regenerator temperature at 900°C. This design is intended to reach a capture efficiency of around 90%, depending on sulphur content, as previously stated.

The preheating of the incoming O_2 is designed to be done with the cooling of the purged material as per the design of Vorrias et al. (2013).

A summary of relevant process data for the simulation of the calcium looping section is presented in Table 3 below:

Table 3: Process data for calcium looping model

Simulation data	
Temperature in carbonator	650°C
Temperature in regenerator	900°C
Molar ratio of $CaCO_3$ to CO_2	7
Molar ratio of make up $CaCO_3$ to CO_2	0.1
Coal flow for regeneration	0.80 kg/s
Flow of oxygen for regeneration	1.76 kg/s
Efficiency of capture	89.99%

7.2.1.3 Compression

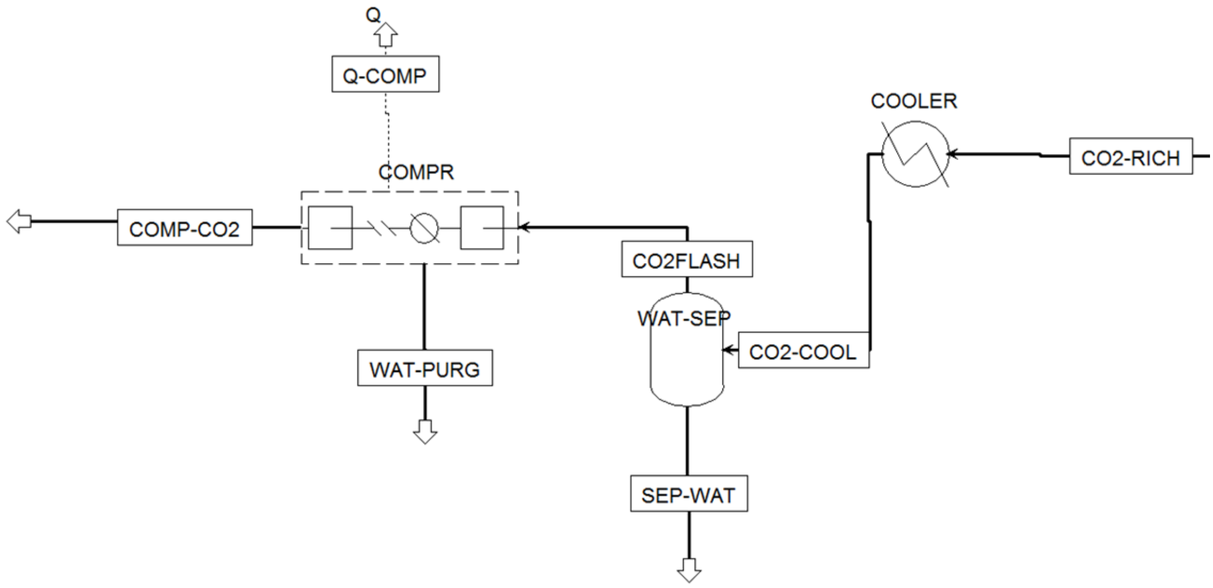


Figure 12: Compression section

The compressions section was set-up with a flash tank to separate the water from the CO_2-rich flue gas before being compressed in a two-stage compressor with intercooling of the gases. Some additional water content is purged from the flue gas in between the stages in the compressor.

In this simulation the CO_2-rich flue gas is compressed to 80 bars in the compressor, leaving the possibility to raise the pressure by pump to match e.g. piping requirements, as done by Hektor (2008). Any additional treatment to the CO_2-rich flue gas beyond compression, such as raising CO_2 purity level, is considered beyond the scope of this thesis and has not been taken into account.

The compression section in this thesis gives out a flow of approx. 176 kg/s compressed CO_2 at 20°C and 80 bars, the purge and separation of water being at a total of 14.6 kg/s.

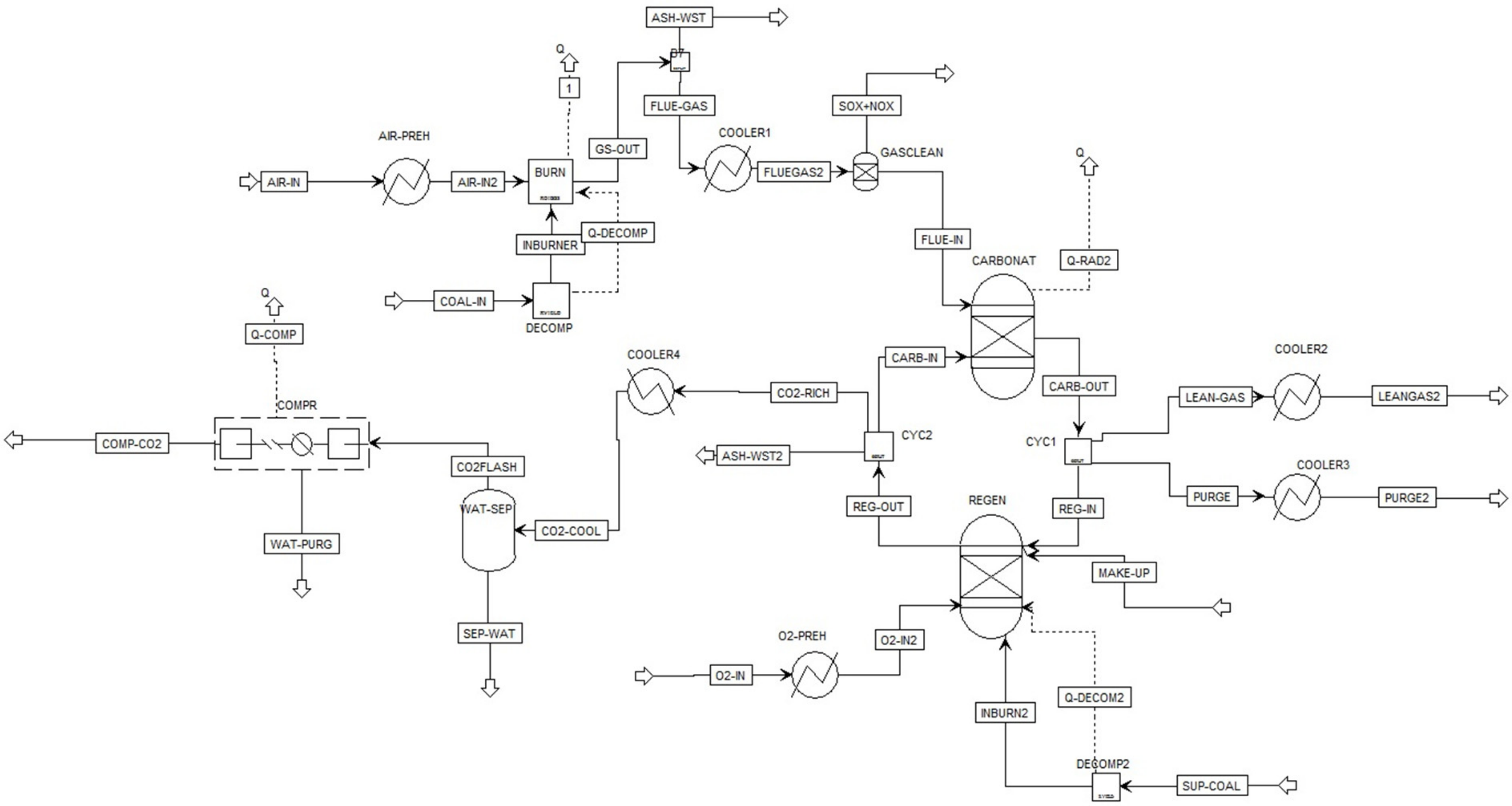


Figure 13: The whole process flow sheet for the calcium looping model with the coal power plant

7.2.2 Reference coal power plant

For the base case power plant a simplified version of the power plant Nordjyllandsværket (NJV) unit 3, located in northern Denmark is taken.

This unit is fired by pulverised coal and producing heat and power. The main plant parameters are shown in Table 4 and indicate the design condition although can vary depending on the operating mode. For this case the operation mode “Nominal load without district heating” was chosen.

Table 4: main operation parameters of NJV unit 3 (Hardarson, 2008)

	Condensing mode (only power production)
T_{CW} [°C]	15
W_{el} [MW]	407.8
η_{th} [%]	47

This plant was chosen due to its modern technology, which makes it to one of the highest efficient operating power plants in the world.

For time for the project a simplified version is necessary. This simplified model was built on given input data from the original NJV. This data is presented in Table 4 and Table 5. More detailed data we achieved from a steam cycle model in EBSILON Professional used at the Division Energy technology for other projects. The Aspen Plus model will be used as a reference for an even more simplified model in MATLAB and serves for the estimation of the error of the MATLAB model. The MATLAB model will be described in chapter 7.3.2. The additional MATLAB model is needed as due to the superimposition of the steam cycle and the desire to take ideal heat recovery into account for the analysis the requirements of the software lie beyond the specific arrangements of heat exchangers used in Aspen Plus.

7.2.2.1 Steam cycle

The steam cycle in this thesis is a simplified version of the steam cycle of the Nordjyllandsvaerket power plant in northern Denmark. The simplified steam cycle used in this thesis consists of seven turbines, one very high pressure turbine (VHP), one high pressure turbine (HP), three intermediate pressure turbines (IP0, IP1, IP2) and two low pressure turbines (LP1, LP2). The feed water heating is conducted by bleeds from the turbines..

The steam is generated in a double reheat boiler as supercritical primary steam with a temperature of 580°C and a pressure of 285 bars. The steam leaves the following reheat cycle with 580°C. The steam data is presented in Table 5.

The steam leaving the LP turbines is condensed by low temperature cooling water (0 – 20°C). The reference power plant gets cooling water supply from the Liim fjord, its temperature varies with the seasons of the year.

Table 5: Steam cycle data of NJV unit 3 (Hardarson, 2008)

	P [bar]	T [°C]	$\dot{m}$ [kg/s]
Primary steam	285	580	265
First reheat	73	580	232
Second reheat	19	580	210

7.2.2.2 Coal combustion

The coal used in the model the reference coal is “El Cerrejon” from Columbia. This coal has very good requirements to be used in power plants, as it has low ash and sulphur content. Its ultimate analysis is shown in Table 6.

Table 6: coal composition “El Cerrejon”

Material	[wt.%]
C	70.32
H	4.64
N	1.67
O	13.53
S	0.54
H_2O	8.60
Ash	9.31
LHV (raw) [kJ/kg]	26271

7.2.2.3 Flue gas

The flue gas cleaning consists of SO_2 and NO_x removal and an electrostatic separator (ESP) with high efficiencies. The flue gas cleaning is important for the success of the calcium looping process integrated in the flue gas train. The data of the flue gas cleaning devices in the NJV can be found in Table 7. The data was chosen to be the same as the data of the devices in the flue gas train of the reference plant. The flue gas cleaning train was also modelled in Aspen Plus as the exact flue gas composition is relevant for the success of the calcium looping process. A simplification was chosen by replacing the exact devices by simple separators which remove particles, NO_x and SO_2 with the efficiency given in Table 7.

Table 7 Flue gas train data (Hardarson, 2008)

	η in % removal
Electrostatic precipitator	99.9
Selective catalytic reduction	80
Flue gas desulphurisation	98

7.2.2.4 Data from the Aspen Plus model

Due to a simplification of the original NJV the values used in the model changed a bit. The aim was to keep the same temperature and pressure levels in the turbine inlets and outlets as well as the produced electricity. The bleeds were reduced due to a simplification of the model to representative bleeds and to still provide a heat transfer to the feed water heating system. Bleeds can now be found after each turbine as long as no reheating cycle follows. Therefore an efficiency drop is noticed. According to these changes the mass flow of coal and circulating steam in the steam cycle needed to be adjusted. This is shown in Table 8, where the detailed data from the model is presented. The model can be found in Figure 14.

Table 8 Aspen Plus model data

	P [bar]	T [°C]	ṁ [kg/s]
Coal consumption	-	-	39.67
Primary steam	285.00	580	254.58
First reheat	73.00	580	254.58
Second reheat	19.00	580	254.58
Intermediate turbine	7.23	355	221.95
Low pressure turbine 1a	0.71	108	97.55
Low pressure turbine 1b	1.51	179	103.58
Condenser	0.03	28	201.13
Flue gas before air heater	1.00	377	401.22
Flue gas after air heater	1.00	109	401.22
Combustion air before air heater	1.00	10	365.33
Combustion air after air heater	1.00	322	365.33
Flue gas to environment/CaLooping	1.00	109	400.81

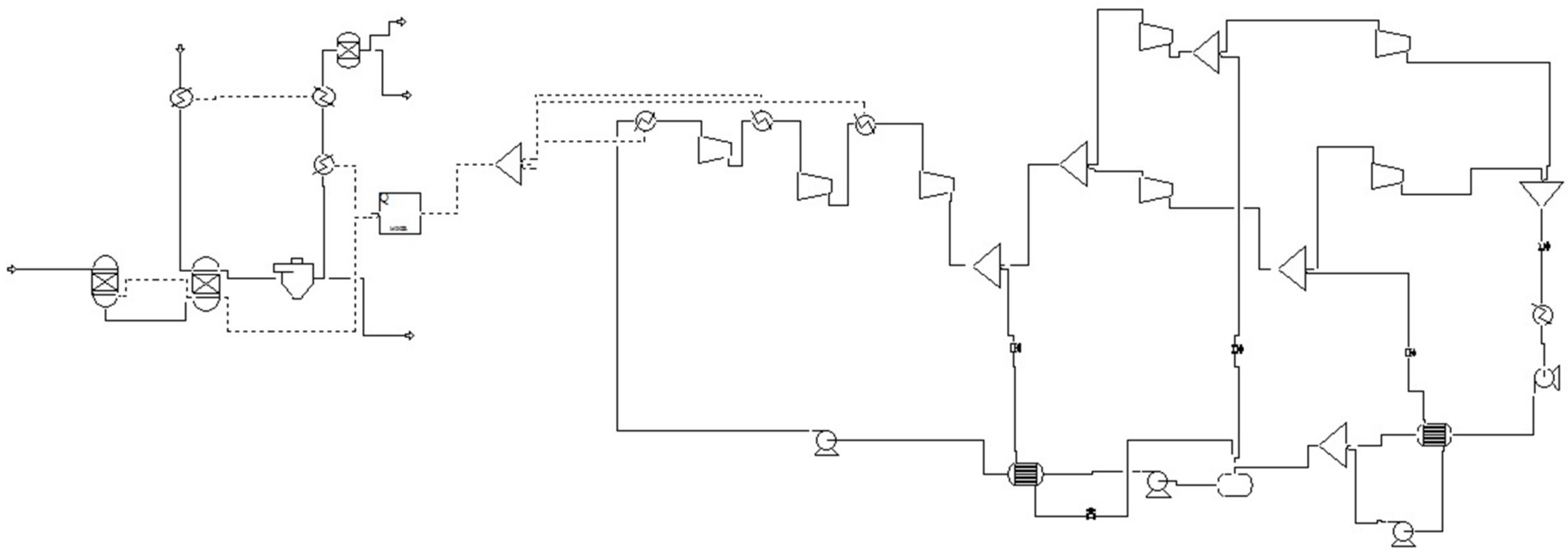


Figure 14: Aspen Plus model of the simplified NJV (case 1.0)

7.2.3 Oxy-fuel combustion model

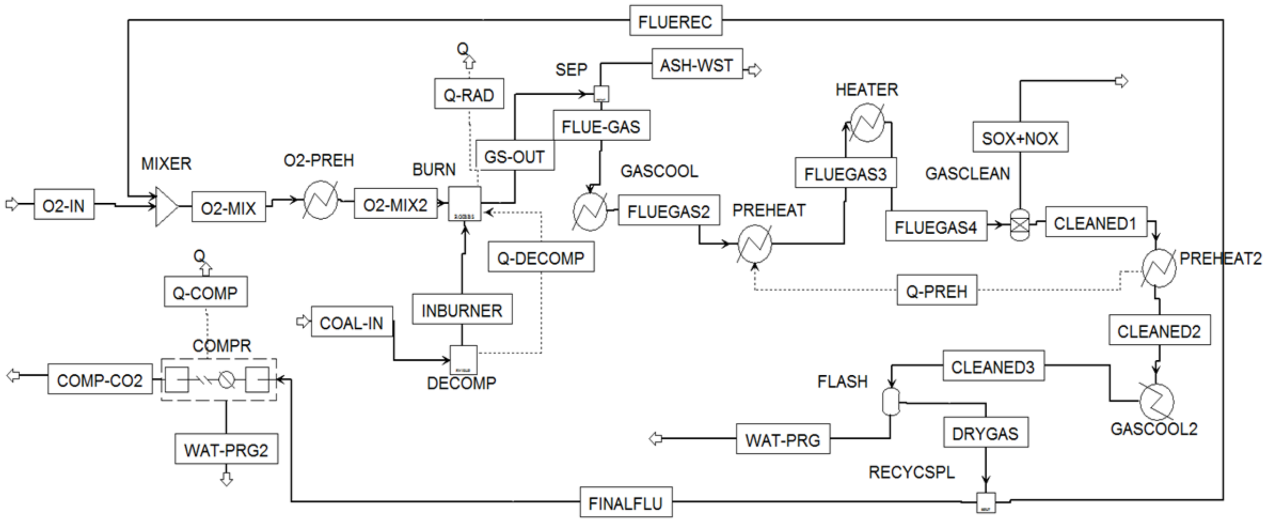


Figure 15: Oxy-fuel plant model

The oxy-fuel model, as shown in Figure 15 above, was modelled using the coal power plant used for the reference with the same coal flow and by adding a recycle stream of flue gas and compression of the CO_2-rich flue gas. The recycle stream of flue gas is mixed with the O_2 stream before entering the combustion chamber. The layout is a simplified version of the set-up shown in Hu (2011) and Rubin et al. (2007), using the values for recycling ratio based on the values cited in their reports. Compression conditions are the same as for the calcium looping model.

A summary of the important values of the oxy-fuel model are presented in Table 9 below:

Table 9: Simulation parameters for the oxy-fuel combustion plant

Simulation data for oxy-fuel plant		
Coal flow	39.67	kg/s
O_2-flow	81.06	kg/s
O_2-temperature	20	°C
Flue gas flow	266.2	kg/s
Recycle temperature	20	°C
Recycle ratio	0.6	-

7.2.4 Cement plant – an interesting integration opportunity

The cement plant is an interesting integration option as it releases a high amount of CO_2 as mentioned in chapter 7.1. The CO_2 emissions result from the calcination of limestone and the combustion of coal to provide the heat to calciner and kiln. The process with its CO_2 sources in calciner and kiln can be seen in Figure 16.

Another interesting point about a combination of cement plant with power plant and calcium looping is that the deactivated sorbent that comes as a by-product of the calcium looping process is not without its uses, as it is possible for this purge of spent CaO to be used in cement production and thus improving the economics of the application of calcium looping. It is possible either to sell the spent CaO as is or integrate the calcium looping with cement production directly and thus capturing even more CO_2 (Blamey et al., 2010).

Either way, this application has a large potential for further reduction of CO_2 as a substantial part (ca 50%) of the carbon emissions in cement production comes from the calcination of CaO from $CaCO_3$. It is important though for the feasibility of cement production that the sulphur content does not get to high as too high sulphur content will worsen the cement quality (Dean et al., 2011).

The process of cement production has a huge demand of CaO and heat supply to heat up the calciner. The heat supply is normally conducted by fuel combustion. The calcium looping can be integrated in this case to capture the CO_2 of both the combustion and the calcination of limestone in addition to generating a part of the CaO for the main process. This integration option is shown in Figure 16 where heat sources and sinks are represented with heaters (arrow up) and coolers (arrow down). While evaluating the integration of calcium looping technology with the cement plant, special attention is then given to the effect that CO_2 capture has on the primary energy demand of the processes.

In a combination of a power plant and a cement plant, it will be investigated to replace all fresh limestone for cement production by the purge of the calcium looping process (in addition to removing a major part of the CO_2 emissions). This means that the energy need for $CaCO_3$ calcination is shared between the two processes, resulting in a reduction in total energy demand for the calcium looping process for both plants compared to if these measures were implemented individually in two separate plants. Even if a total replacement of fresh limestone in the cement plant is not possible (or even if the purge from the coal plant is sold as raw material to a cement plant without calcium looping), a substantial benefit in terms of energy need and CO_2 emissions reduction would still occur. For this reason such a combination of both plants is highly interesting. In such a case, flue gas from both plants will be led to the same calcium looping unit and the purge of CaO from which will be led back to the cement plants kiln.

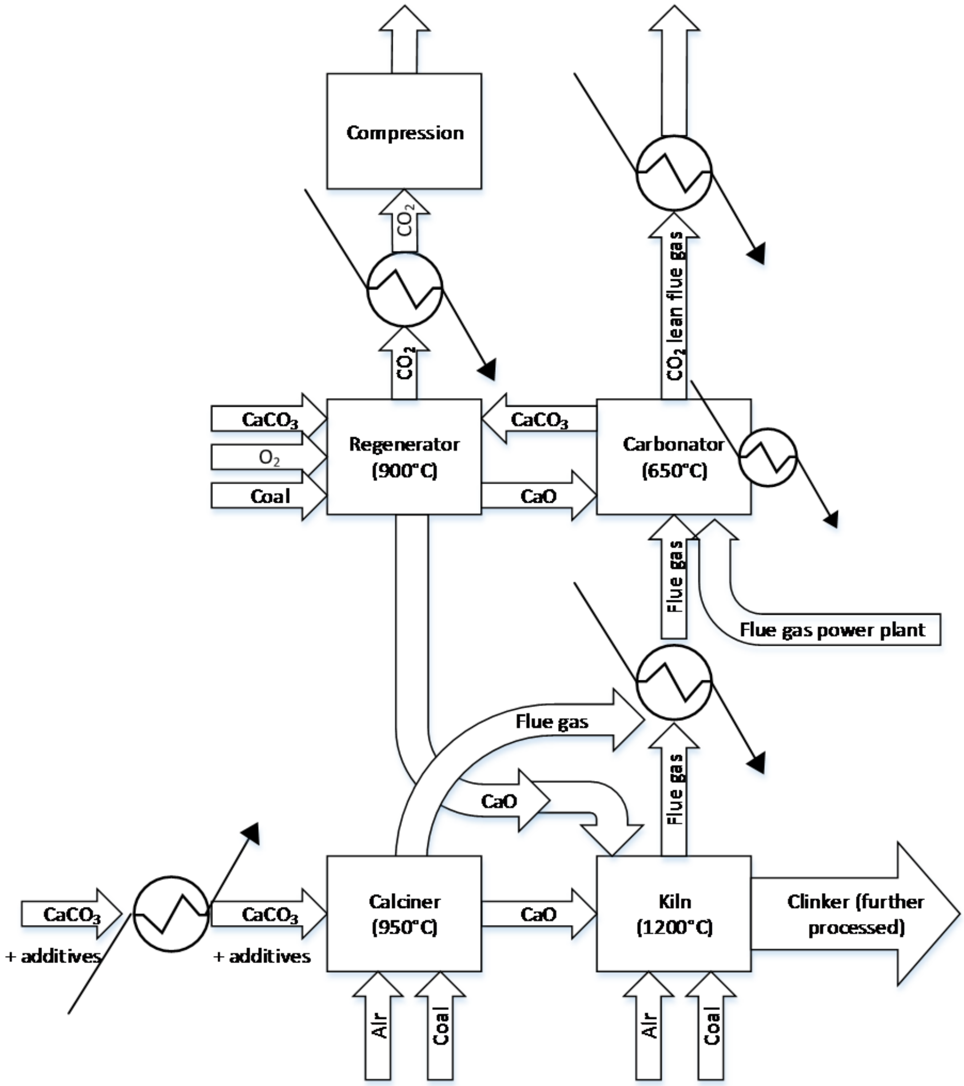


Figure 16: Integration of a calcium looping process into a cement plant

7.2.4.1 Cement plant model

The base case for the cement plant is taken from Benhelal et al. (2012). The Aspen Plus model was set up with the given data to achieve the given values in the literature. Keeping the input values exactly the same as in the literature reference makes it possible to achieve the same output values. Problems to achieve the exact temperature occurred with the coal composition as it is only given in water and ash free conditions. Water and ash free conditions of coal are not the real industrial conditions. Therefore the mass flow of the coal will vary dependent on the used coal and it's pre-treatment, as this will influence the water and ash content of the coal. The composition of the coal is shown in Table 11.

The base case of the cement plant is shown in Figure 17 and the stream data is presented in Table 10. The pressure is constant at 1 bar. For the clinker production a raw material stream of $CaCO_3$, SiO_2, Fe_2O_3 and Al_2O_3 is pre-heated up to 700°C and enters the coal fired calciner for calcination of $CaCO_3$ into CaO as shown in Figure 17 the combustion air consists partly of the preheated air from clinker cooling and partly of flue gas recirculated from the kiln. In a cyclone the solids are separated from the flue gas and the solid materials are transported to the kiln, and the flue gas is released. In the kiln the materials are heated up until a temperature of 1500°C is reached. To deliver this heat a combustion process is needed in the kiln. The combustion air in the kiln is also preheated air from clinker cooling and the flue gases are recirculated to the calciner. The product after the kiln is clinker that needs to be cooled down with air. One part of the air is not used in the described cycle and released to the environment at 1100°C (Benhelal et al., 2012).

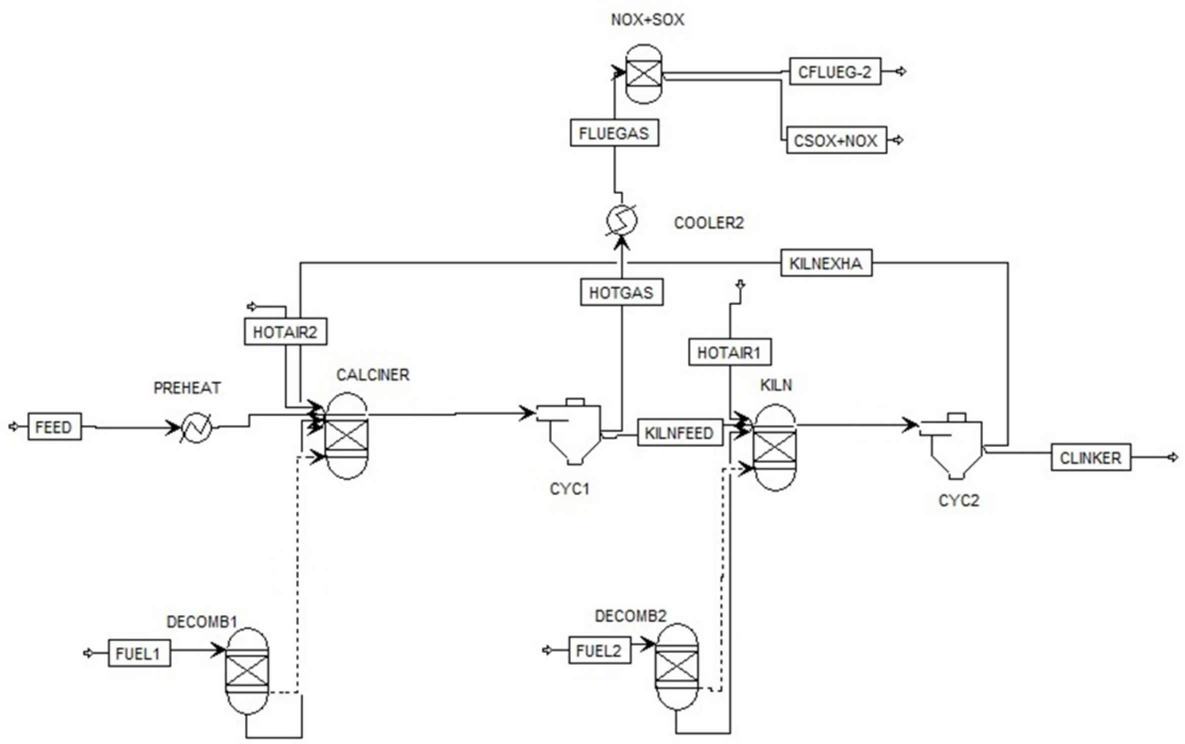


Figure 17: Cement plant model in Aspen Plus

Table 10: Cement plant data (Benhelal, et al., 2012)

Stream	Flow rate [kg/s]	Temperature [°C]
Feed	49.72	50
Calciner Feed	49.72	700
Fuel 1 (coal)	2.08	30
Kiln Feed	33.06	950
Fuel 2 (coal)	1.45	30
Clinker	33.06	1500
Kiln Exhaust	15.98	1500
Hot Air	41.70	1100
Hot Air 1	14.72	1100
Hot Air 2	26.39	1100
Air to Environment	0.59	1100
Hot Gas	62.28	950

A flue gas cleaning is established according to the data from NJV (see Table 7). Usually cement plants have a flue gas train included as well, but no data about the reference plant could be found. For an optimal integration of the calcium looping process the removal of NO_x and SO_x is essential, otherwise the makeup flow of the limestone needs to be significantly higher as the SO_x reacts with the lime and the purge can only be used in the cement production when the contamination of sulphur is very low. Without the removal the values of sulphur contamination will be beyond the boundaries. A removal of both components is also necessary the meet the air pollution restrictions.

The investigations are done on case 2.0 as described above, case 2.a and case 2.b that uses exactly the amount of CaO-purge from the calcium looping.

Case 2.b (limestone free) is achieved with using the same power plant but changing the cement plant. The changes in the cement plant are presented in Figure 18 and described below.

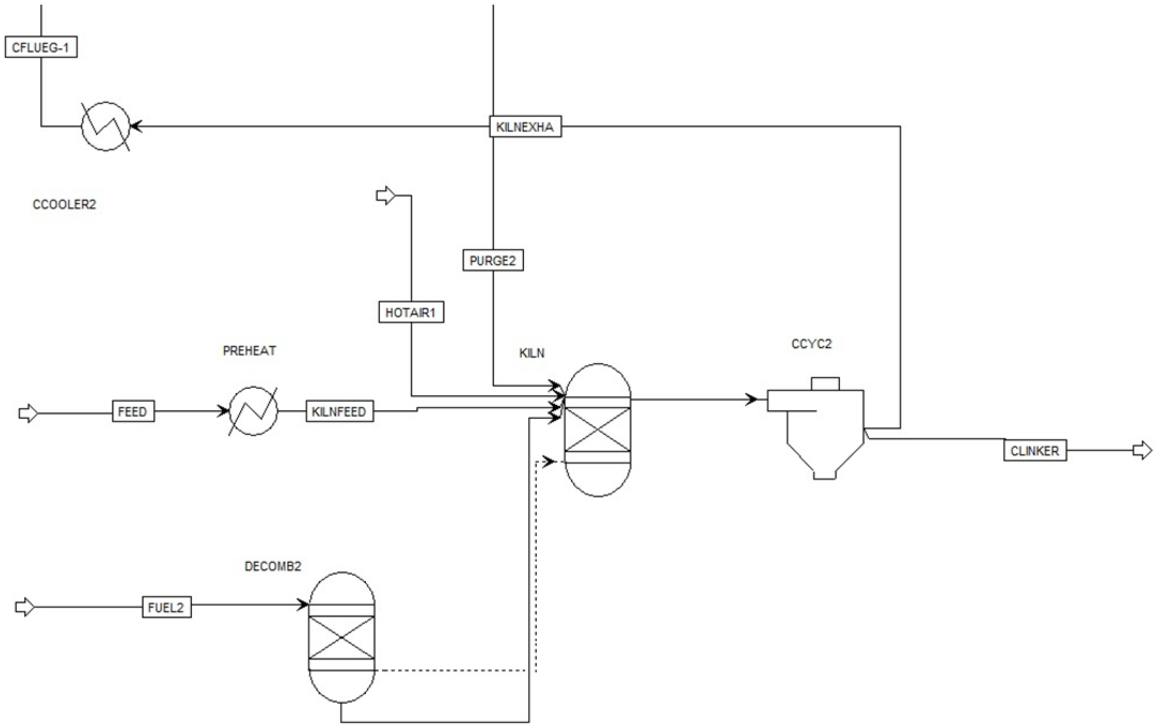


Figure 18: Aspen Plus model of limestone free cement plant (case 2.b)

The feed stream consists now of SiO_2, Fe_2O_3 and Al_2O_3 which are heated up in the preheater to 950°C. The purge from the calcium looping consists mainly of CaO and is equally heated up to 950°C. Both streams get mixed in the kiln. The feed stream is varied according to the amount of purge entering the kiln, so that the composition of the mixture stays the same as in case 2.0. The exhaust gases from the kiln are directed to the calcium looping process. According to the lower amount of material entering the kiln the coal mass flow and the combustion air are calculated and adjusted. The equation to calculate the scaling factor of the whole cement plant is

$$Scaling\ factor = \frac{\dot{m}_{CaO_{kiln\ in_{2.b}}}}{\dot{m}_{CaO_{kiln\ in_{2.a}}}} \tag{6}$$

7.2.4.2 Specific coal data for the cement plant

The coal[1] used in the cement plant is chosen to be the same as in the literature reference as all input data is chosen from that source. The coal differs from the coal used in the model of the NJV. The coal composition is shown in Table 11.

[1] This coal needed to be used for the reference as not all detailed cement plant data were available but the exact data from the literature reference was taken. The coal power plant model and the calcium looping model were already modelled with the coal “El Cerrejon” as described before, when it was realized that exactly this coal is needed for the cement plant. A change in the existing models would have been too demanding.

Table 11: coal composition reference coal (Benhelal, et al., 2012)

Material	[wt.%]
C	80.33
H	4.83
N	1.84
O	11.40
S	0.60
H_2O	0
Ash	0
LHV (raw) [kJ/kg]	30560

7.2.4.3 Validation of the models

The stream composition of the product streams matches good with the reference. But not all numbers for all streams in the cement plant are given in the reference. The coal composition was only given in ash and water free conditions which are not the industrial conditions. The same way a detailed flue gas composition was missing and not all reactions in the reactor could be modelled due to limitations of Aspen Plus. The heat generation in the calciner and the kiln might therefore vary in reality. Using heater and cooler the given temperatures of the streams are achieved, so that the head loads for heat transfer to the steam cycle are still correct. Merely the coal consumption is influenced by this error potential. Due to this problem the coal and air flow could not be adjusted perfectly for a change of the reference cement plant. For a connection of the cement plant with calcium looping the raw material stream in the calciner is reduced about 43%. As the coal flow under industrial conditions it not known the reference coal flow was reduced about 43% as well as the combustion air. The same calculations are done for the limestone free cement plant, but due to the reduced total amount of clinker and the no longer required calciner the coal flow in the calciner was set to 0 and in the kiln reduced about 50% as the raw material stream is reduced about this amount, the combustion air is proceeded the same way.

Another aspect for the validation of the results is the comparison of the electrical efficiency of the coal power plant model in Aspen Plus and MATLAB. The model in Aspen Plus has an electrical efficiency of 40.1% and the model in MATLAB an electrical efficiency of 42.8%. The efficiencies of both cases differ about 2% and show a high improvement potential of the Aspen Plus model. Considering the ideal heat transfer in the MATLAB model the better result for this model is reasonable.

7.3 Process integration

As shown in the above sections, the calcium looping technology for CO_2 capture is based on the reaction between carbon dioxide (CO_2) and lime (CaO) to form limestone ($CaCO_3$) and subsequent release of carbon dioxide by reversing the reaction in the calciner. The first reaction is exothermic and occurs at around 650°C and the second is endothermic and occurs at high temperature. Additionally, as already shown in Figure 16 above, flue gases, oxygen and carbon dioxide require heating and cooling in different locations.

The application of the calcium looping for carbon capture either in coal power plant or in a cement plant has a significant impact on the overall energy consumption of plant which can be minimized by appropriate heat integration. The main objective of this work is in fact to investigate the thermal behaviour of the calcium looping technology and to highlight key process integration aspects that could favour the adoption of such technology for carbon capture in a coal power plant also in combination with a cement plant.

For this purpose, pinch analysis is used which allows to discard a specific arrangement of the heat exchanger network and to estimate ideal thermal integration between heat sinks and heat sources.

In this chapter the method and assumptions used for the process integration of the calcium looping technology in the selected processes will be presented and explained.

The process integration analysis is organized in the following way:

1. The thermal cascade[2] of the calcium looping process only is estimated.
2. The integration of the calcium looping with the coal power plant is investigated. To this end a steam cycle model based on superimposition of elementary cycles was used in order to find optimal steam mass flow rates that matches different configurations of coal combustions (with and without calcium looping, oxy-fuel, etc.) using similar steam parameters. In particular, different heat integration options are analysed based on different practical limitation to ideal heat integration.
3. The integration of the calcium looping with the coal power plant and a cement plant of different sizes was investigated.

[2] Graphical presentation of net surplus/deficit of heat in the process

7.3.1 Calcium looping Grand Composite Curve

The calcium looping process is a net exothermic process, which under constant operating conditions will generate a constant amount of excess heat. As such it can be considered a background process upon which a steam cycle can be fitted as a foreground process.

The available heat from the calcium looping process comes primarily from the warm flue gases leaving the carbonator and the regenerator respectively, as well as the heat from the exothermic reaction in the carbonator (which is represented by the vertical line at 650 °C in the figure below). Some heat is also available from the purge stream of spent sorbent. A heat demand also exists for the oxygen stream coming from the air separator. The result of putting all of this together into a GCC is shown in Figure 19 below:

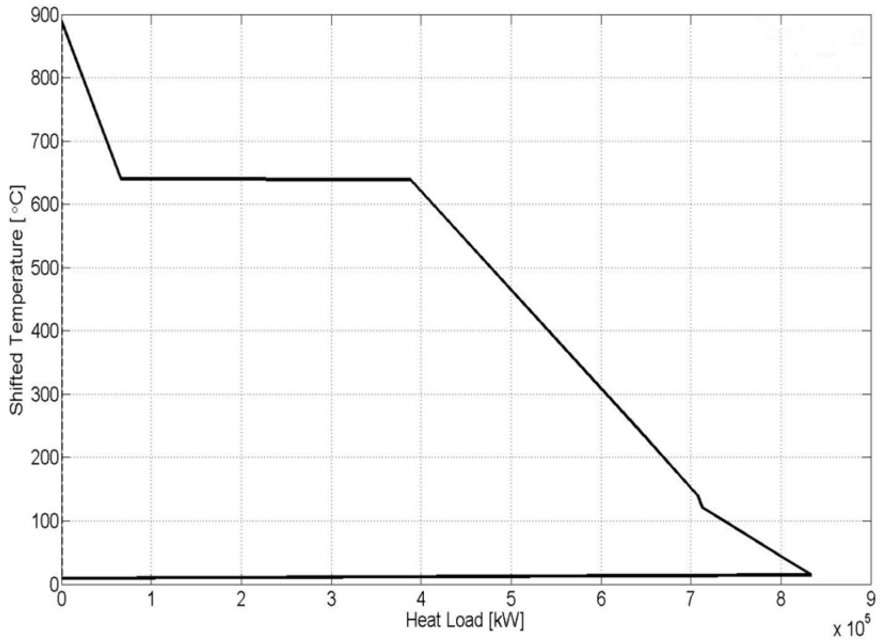


Figure 19: GCC of calcium looping process

The GCC in Figure 19 above is for the calcium looping process as a separate process, if for example the coal power plant process is included with the calcium looping process for the scope of the background GCC it will change accordingly to accommodate the available energy from both these sources. Examples of this will come later in the thesis when the heat from both coal combustion and calcium looping will be integrated with a single steam cycle.

7.3.2 Modelling of steam cycles by superimposition of elementary cycles

As shown in the section above, the calcium looping where the heat for calcination is provided by oxy-fuel combustion is essentially an exothermic process since heat is available from combustion (at the net of the calciner heat demand) and from the carbonator (which is exothermic). The integration of the calcium looping with a coal power plant therefore consists on making available this heat for generation of extra steam which can be expanded in a new turbine section thus providing extra power in addition to the power already generated in the reference power plant. The objective of the present analysis is therefore to estimate the electrical efficiency (the ratio between the total net generated power against the total coal input) of the coal power plant with and without carbon capture (calcium looping and oxy-fuel). While the aspects of such integration are discussed below in a dedicated chapter, it is necessary to firstly introduce another tool of our investigation which was used to conduct such analysis.

The successful design of a coal power plant is substantially a matter of optimal thermal integration of the steam cycle with the heat available from coal combustion at different temperature and partially also of integration of air preheating and fuel gas cleaning sections.

The approach followed in this work is to fix the coal flow rate and the characteristics of the coal combustion as in the reference base case (NJV) and then compare the power generation potential (i.e. electrical efficiency at constant fuel) under the conditions of maximum heat integration. This allows highlighting the penalty introduced by different carbon capture options independently on the specific arrangement of the heat exchangers (e.g. of how feed water preheating and air preheating are realized in practice).

The focus is therefore on the maximization of the steam cycle integration against given heat availability from coal combustion, flue gas cleaning, and calcium looping when in place (constant grand composite curve).

A rigorous mass and energy balance of the reference plant (NJV) was provided above, although based on a simplified layout of the steam bleeds from the turbine as compared to the actual plant. Here a new steam cycle integration (design) is proposed based on a further simplified model of the steam cycle based on superimposition of elementary cycles, as explained in Morandin et al. (2013) and Toffolo (2014). This approach is based on the decomposition of a steam cycle with multiple steam bleeds from the steam turbine into a combination of elementary steam cycles consisting on compression, evaporation, expansion and condensation.

Accordingly, a steam cycle consisting of condensing turbine with one steam draw-off at an intermediate pressure is represented as a superimposition of two steam cycles sharing the same evaporation pressure (and temperature-heat load profile) and having two different condensation pressures (respectively the condenser and at the steam draw off pressure). The compression and expansion steps are divided in two compressions and expansions each belonging to one elementary cycle. In so doing, the original steam cycle mass flow rate is divided into mass flow rate contributions each belonging to one cycle.

The thermodynamic analysis of the steam cycle, and therefore its integration, can be conducted as the composition of the elementary cycles and the total net power of the original cycle can be estimated as the sum of the power of elementary cycles, as well as the heat load for steam generation can be estimated as the sum of the heat loads of steam generation in elementary cycles. While this procedure introduces some errors compared to a rigorous model of the steam cycle as expansion with multiple steam bleeds is not equivalent to multiple turbines working across different enthalpy drops, it is possible to choose appropriate points of the steam cycle where the steam thermodynamic state can be made equal to isothermal (and isenthalpic) mixing of the steam mass flow rates of the elementary cycles in order to minimize such errors (this is discussed later in more detail for the actual cycle of the reference power plant).

The above approach may be seen just a complication of the analysis of a steam cycle unless an intrinsic property of the energy balance is exploited: all heat and power loads can be represented as the product of the steam mass flow rate with the enthalpy difference between two steam cycle points. Accordingly, by holding constant the state of the steam (e.g. temperature, entropy) in the key steam cycle points, the energy balances can be represented as a set of linear equations where the steam mass flow rates of the elementary cycles are the only linear variables.

Now, given the thermal cascade of the coal combustion plus all the other thermal streams that depends only on the coal combustion (and that are therefore constant), the integration of the steam cycle can be studied as a linear programming problem where the steam mass flow rates are the linear variables, the objective function is the power generation, and the constraints are set by the thermal cascade (positive cumulative heat load at each temperature interval).

This is equivalent to find the shape of the steam cycle grand composite curve (variable grand composite curve) that matches the shape of the constant grand composite curve as typically done by the so-called background, foreground analysis. The additional contribution of the above approach is that the integration can be studied with mathematical tools (here in MATLAB) and therefore automatized made faster. In particular, the framework is used in this work to perform such analysis which has been developed at the Div. of Heat and Power Technology.

7.3.3 Identifying elementary steam cycles

The original steam cycle (as indicated in the simplified version of the NJV power plant discussed in chapter 7.2.2) can be defined by defining a number of points in a T-s diagram which will represent the thermodynamic state of the steam (water or vapour or mixture of two) in key cycle points. For each point pressure, temperature, entropy and enthalpy are specified in a MATLAB spreadsheet according to the MAT4PI tool.

The MAT4PI tool has several background files to enable computation, but two files have been used actively in this thesis. One is the "description" file which is used for building the process description, i.e. defining the streams in the system (temperature, heat load etc.) and where they belong (defined by assigning the streams to groups). In this file the choice of steam cycle is done and parameters such as isentropic efficiencies can be chosen.

The other file is the "steamcyc1rr5" file, where the steam cycle is defined. All key cycle points are defined one by one by entering information about pressure, enthalpy and temperature. This is followed by construction of each of the elementary steam cycles. The elementary steam cycles are constructed by defining which key cycle points are included in each elementary steam cycle and in which order. Three different steam cycle files have been used in this thesis, each with its own name, differing only in the amount of reheats used.

The steam cycle can be customized in any way that the user wishes by defining the points on the graph to fit the relevant circumstances. In cases such as the reference plant in this thesis, which are operating at super critical pressure levels for the steam, care must be taken in defining the points in the T-s diagram as the evaporation does not follow the same isothermal entropy increase as for lower pressure levels.

The T-s diagram for the advanced steam cycle in this thesis is presented in Figure 20 below and a process schematic of this steam cycle is presented in Figure 21.

When the steam cycle is defined and the heat flows of the investigated system are put in, the program calculates the steam mass flow rates that maximize the heat integration and accordingly the power generation. Curves are also generated.

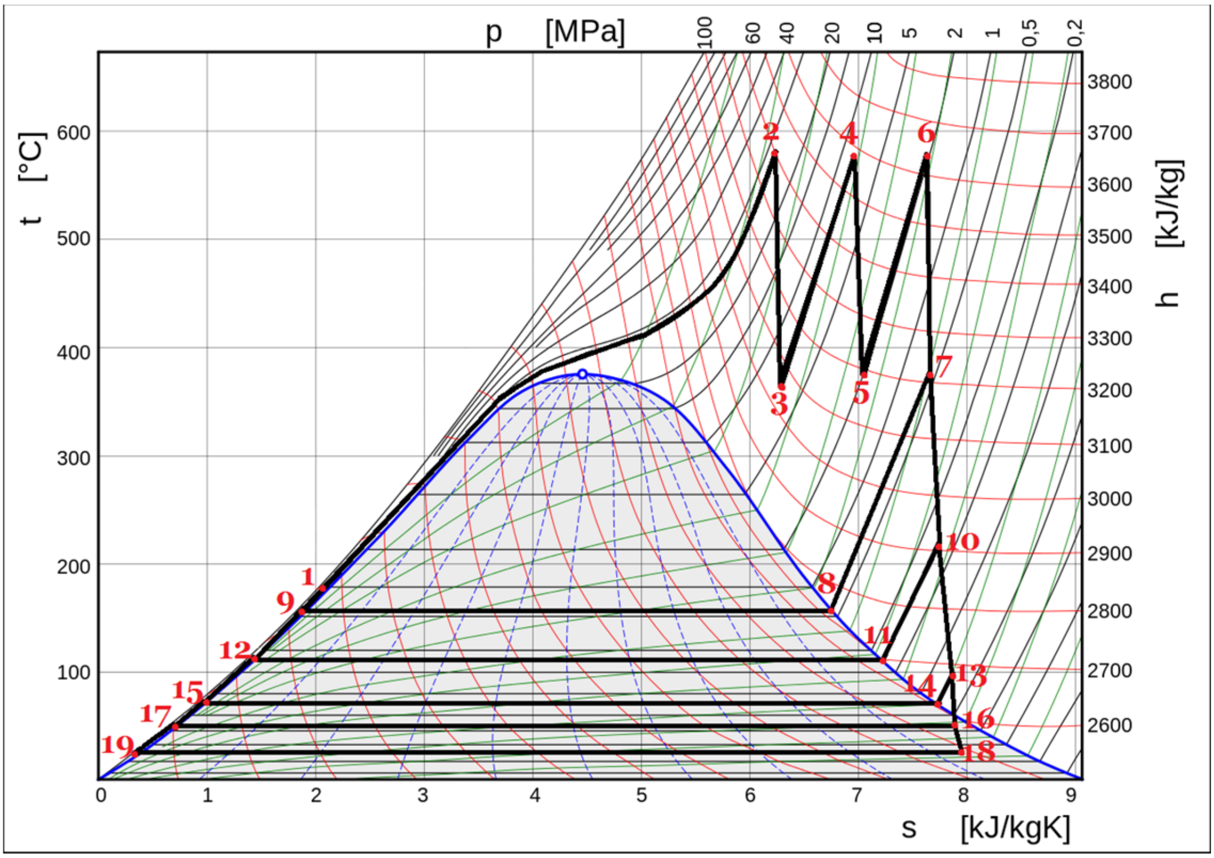


Figure 20: Representative T-S diagram for the double reheat steam cycle modelled in MATLAB

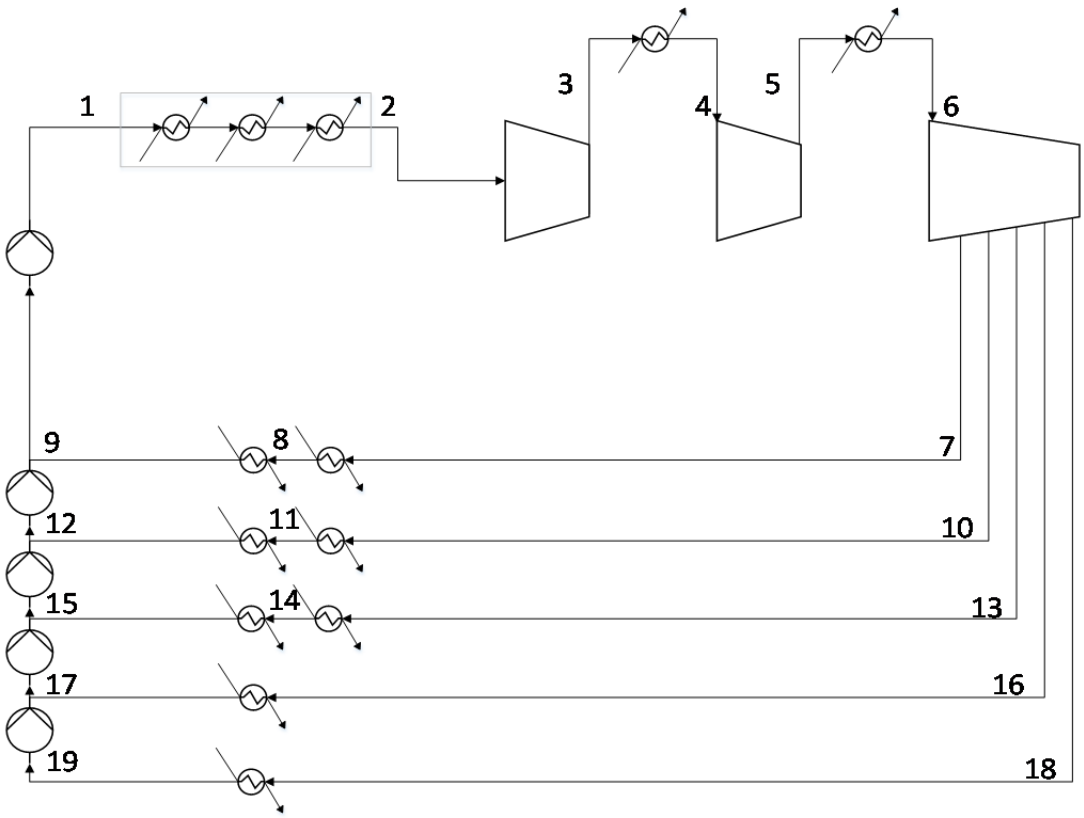


Figure 21: Steam cycle of the base case power plant (numbers according to Figure 20) according to approach based on superimposition of elementary cycles.

7.3.4 Analysis for coal power plant with calcium looping

Two possible options for the steam cycle integration are investigated: (a) integration of a separate steam cycle with the calcium looping process, (b) integration of a single steam cycle with the whole coal power plant plus calcium looping process, as shown in the pictures, where the main heat flows are shown in red. In the case with two separate steam cycles, two different levels of complexity will be investigated for the steam cycle used for the calcium looping process. One set-up (case 1.a) will use a simple steam cycle for the calcium looping without any reheat stages and only the standard five bleeds from the turbine as for the reference coal power plant. The other set-up (case 1.b) will also include a reheat after the first turbine stage.

The carbonator is a source of heat due to the exothermic reaction which releases a large amount of heat and therefore needs to be cooled down. Moreover heat can be recovered from the CO_2 lean flue gas stream, leaving the calcium looping cycle at around 650°C and the CO_2 stream leaving the regenerator at 900°C which needs to be cooled before compression and storage. Overall, heat can be recovered from high and medium temperature levels and steam can be produced for power generation in a steam turbine set in addition to that of the basic power plant. This option (case (a)) is the most common for cases of retrofitting of existing plants.

For a new designed power plant, the integration of a single steam cycle may be explored where the net heat released by calcium looping is used to produce high pressure and high temperature steam in combination with the upstream coal combustion to feed the same turbine set.

The objective of the investigation around the coal power plant is therefore to estimate the overall impact of the calcium looping technology by comparing the electrical efficiency of the two plant integration options with calcium looping (case (a) and case (b)) with the base case without calcium looping using the previously described methodology. As a point of reference one case with oxy-fuel combustion technology will also be analysed. All these cases will be investigated with the same heat integration method (Pinch Analysis).

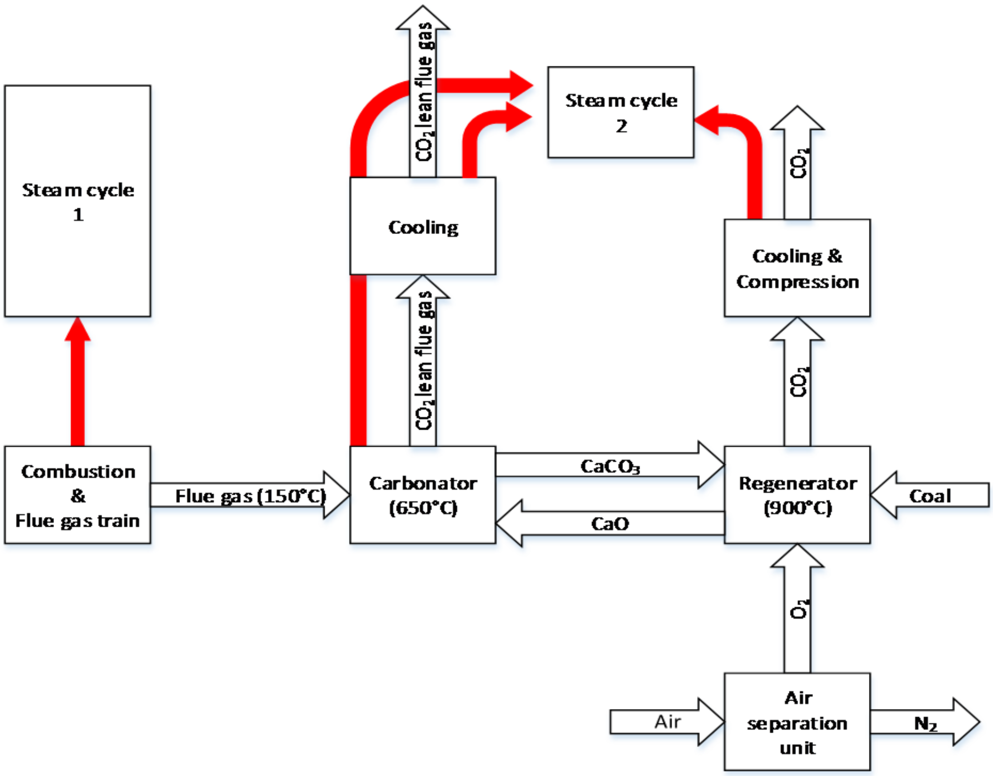


Figure 22: Power plant with calcium looping integration and second steam cycle

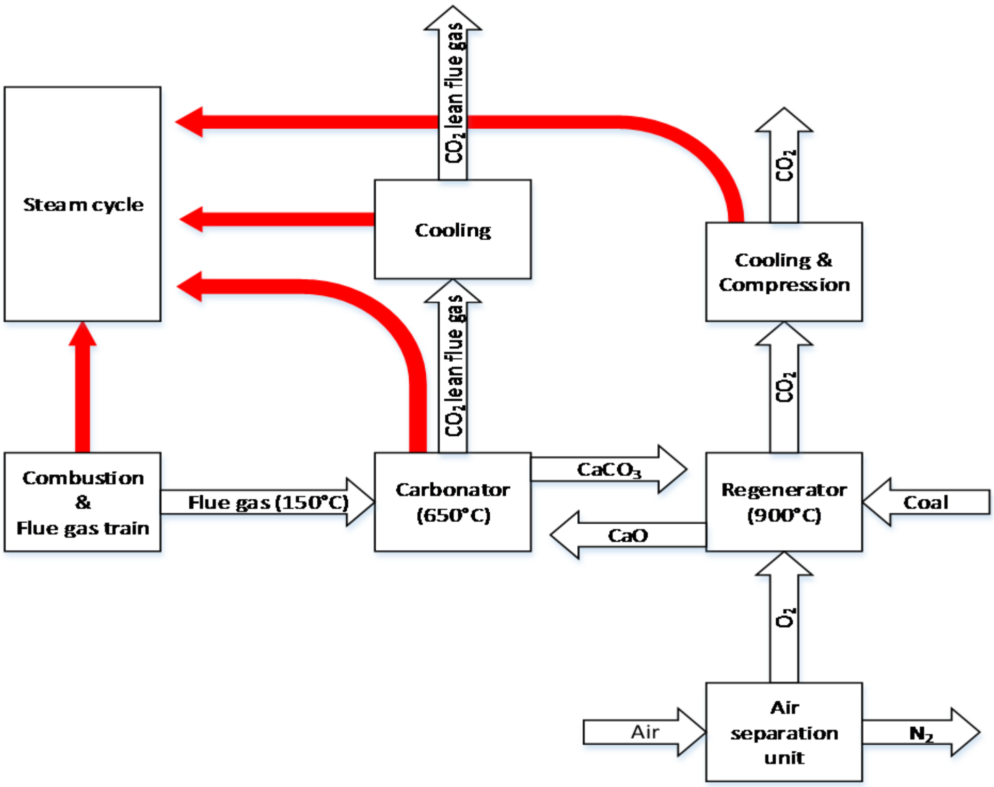


Figure 23: Power plant with calcium looping integration in one steam cycle

7.3.5 Analysis of the coal and cement plants

The heat sources in the cement plant are the flue gas at the exit of the calciner and the hot air after cooling down the clinker that is lead to the environment. The flue gas exits the calciner at a temperature of 900°C and needs to be cooled down before it is released to the environment or redirected to a calcium looping process. The hot air of the clinker cooling has a temperature of 1100°C and can be reused as well. This heat sources deliver heat on a high temperature level that can be used for steam generation in a steam cycle for power production via steam turbine.

For a combination with power plant and calcium looping it is expected that the available heat sources in the calcium looping process are rising due to a higher amount of hot gases. Therefore the objective of the investigation are the base case cement plant (2.0) and the combined cement plants with power plant and calcium looping (cases 2.a and 2.b). Since the integration into one steam cycle for power plant and calcium looping was the best solution this is the only solution investigated for the cement plant cases. The investigations are again conducted with Pinch Analysis.

8 Results and discussion

In this chapter the results of the calculations in MATLAB are presented, compared with each other and discussed.

8.1 Coal plant/reference case (Case 1.0)

Using the thermal stream data for the reference coal power plant (as presented in Table 12 below) a process integration of the coal combustion with a steam cycle is done with help of MAT4PI. This is done as to get a reference case using the same procedure and with the same assumptions for the steam cycle as the other cases that are investigated.

The results from these calculations for the reference coal power plant can be seen in Figure 24 below, with the most important parameters presented in Table 13.

Table 12: Stream data for case 1.0

Stream	Temperature in [°C]	Temperature out [°C]	Heat load [kW]
Coal plant			
- Radiative heat in boiler	1000	1000	562 044
- Convective heat from flue gas	1000	150	404 860
- Air preheating	25	323	117 316

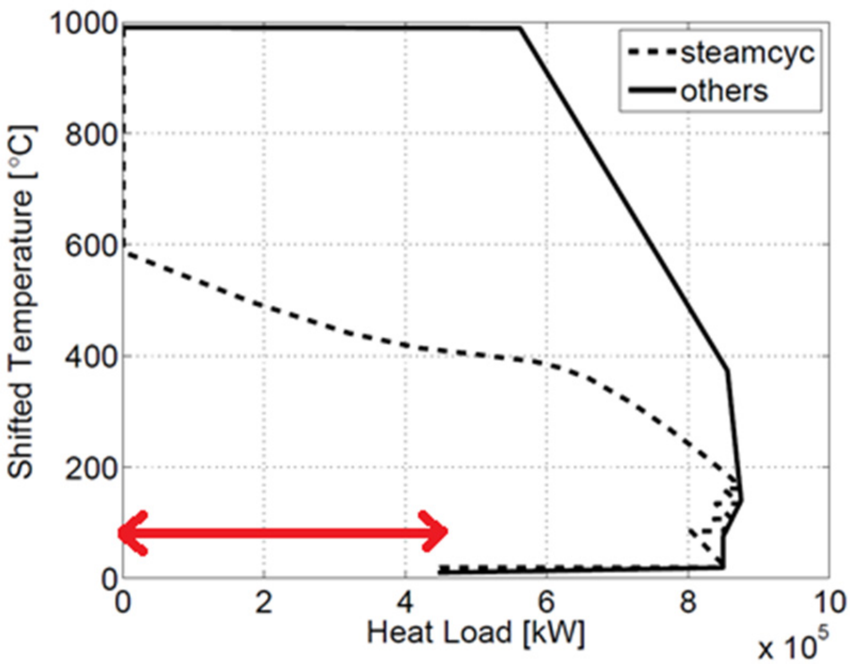


Figure 24: Grand composite curve for the reference coal power plant

In Figure 24 the thick black line represents the background process, i.e. the heat from the coal power plant, and the dotted line represents the steam cycle. The zigzag pattern of the dotted line to the right of the figure represents the draw-offs from the turbine at the different pressure levels and the expansion of the steam. The marked range in the bottom left (in the figure above shown with a red double arrow) represents the available energy which is not used in the system itself, i.e. the net output of the system.

The main results of the coal power plant model are presented in Table 13 below, with the energy input being calculated from the coal flow and the heating value of the coal as previously presented in the process modelling chapter:

Table 13: Results of the thermal integration of the reference power plant in MATLAB

Results from thermal integration		
Energy input (coal)	1042.3	MW
Energy output (electricity)	445.6	MW
Electrical efficiency	42.8	%

Here it can be seen that the efficiency of the reference power plant is lower than the previously stated efficiency of Nordjyllandsvaerket (page 24). This is due to that the steam cycle that is used in this process integration is a simplified version of the very advanced steam cycle that is used in Nordjyllandsvaerket. These results, which are presented here above, are the reference point for all other cases going forward.

8.2 Coal power plant with calcium looping

For the integration of the calcium looping with the coal power plant, two main alternatives were considered: 1) a system with two separate steam cycles, one for the coal power plant and one for the calcium looping unit, and 2) an integrated system using only one steam cycle for both processes. This is equivalent to conduct to separate heat integration analyses: one in which two steam cycles are integrated with two separate background grand composite curves, and one in which a single background curve is used and only one steam cycle is considered.

For the calcium looping process some auxiliary electricity has to be provided for the compression of the CO_2 and the separation of O_2. The energy for compression was given in the simulations from Aspen, but the value for the energy needed for O_2 separation was calculated using the flow of O_2 given from Aspen and the value of 0.25 kWh/kg O_2 (Fu C, Gundersen T. Power reduction in air separation units for oxy-combustion processes based on exergy analysis. 2011;29:1794-8.).

8.2.1 Thermodynamic stream data for coal power plant and calcium looping process

All of the different configurations of calcium looping added to a coal power plant that are presented in this chapter uses the same thermodynamic streams and differ only in the integration, and complexity, to the steam cycle. All of the thermodynamic streams used in MAT4PI to model the integration are presented in Table 14 below:

Table 14: Thermodynamic stream data for coal plant and calcium looping process

Stream	Temperature in [°C]	Temperature out [°C]	Heat load [kW]
Coal plant			
- Radiative heat in boiler	1000	1000	562 044
- Convective heat from flue gas	1000	150	404 860
- Air preheating	25	323	117 316
Calcium looping process			
- Convective heat from CO_2-rich stream	900	20	233 517
- Radiative heat from carbonator	650	650	321 162
- Convective heat from CO_2-lean stream	650	150	182 166
- O_2-preheating	20	100	5 189
- Purge stream of spent sorbent	650	252	5 189
- Cooling in compression unit	259.4	20	118 093

8.2.2 Separate steam cycles (cases 1.a & 1.b)

For the case with two separate steam cycles one for the coal power plant and one for the calcium looping unit, the question arises how advanced the configuration of the steam cycle for the calcium looping process (which in the case of a retro-fit would be a new investment) should be. Two cases were considered, one with a simple steam cycle with 5 draw-offs and one a bit more advanced using also reheat of the steam to raise efficiency.

In Figure 25 the grand composite curve of the simpler steam cycle for the calcium looping process is shown. The calcium looping available heat profile can be seen in the black thick line, where the horizontal part at 650 °C is the heat from the carbonator, and the rest is convective heat transfer from the flue gases (both CO_2 rich and CO_2 lean streams), O_2 preheating, cooling in the compression unit and the purge stream transferring spent sorbent away from the process..

The grand composite curves for the calcium looping process using a steam cycle with single reheat is shown in Figure 26.

The difference between these two configurations lies only in the steam cycle while the temperature-heat load curve for the calcium looping is identical.

The main results are summarized in Table 15 below:

Table 15: Results of the thermal integration of calcium looping to a separate steam cycle

Results for calcium looping and total plant		
Total process energy input	**1875.2**	**MW**
- Energy input for calcium looping	832.9	MW
Auxiliary electrical consumption (compression + O_2-separation)	139.1	MW
- Compression	79.5	MW
- O_2-separation	59.6	MW
Case 1.a		
Total process net energy output	591.6	MW
- Energy output from calcium looping	288.2	MW
Total electrical efficiency	**31.8**	**%**
Case 1.b		
Total process net energy output	643.1	MW
- Energy output from calcium looping	339.7	MW
Total electrical efficiency	**34.4**	**%**

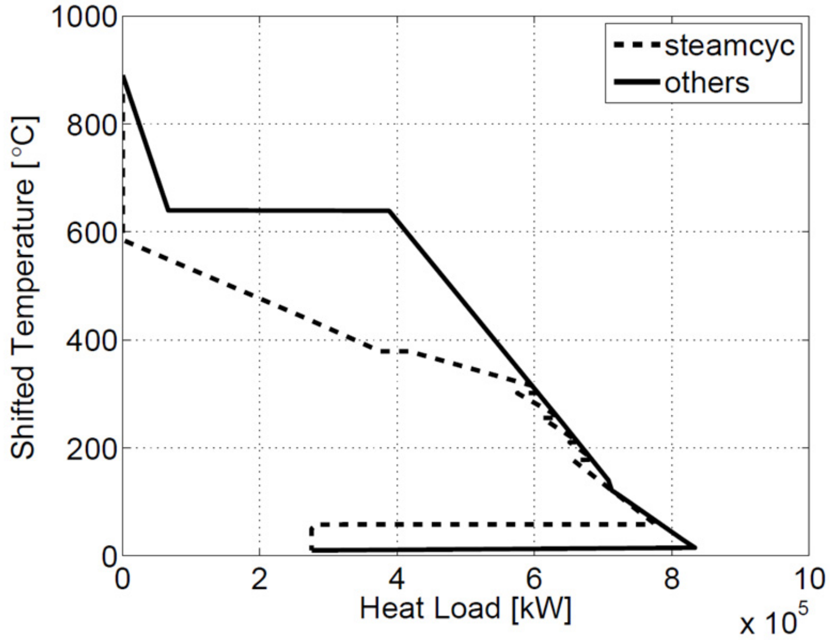


Figure 25: Grand composite curve for calcium looping process with a simple steam cycle (case 1.a)

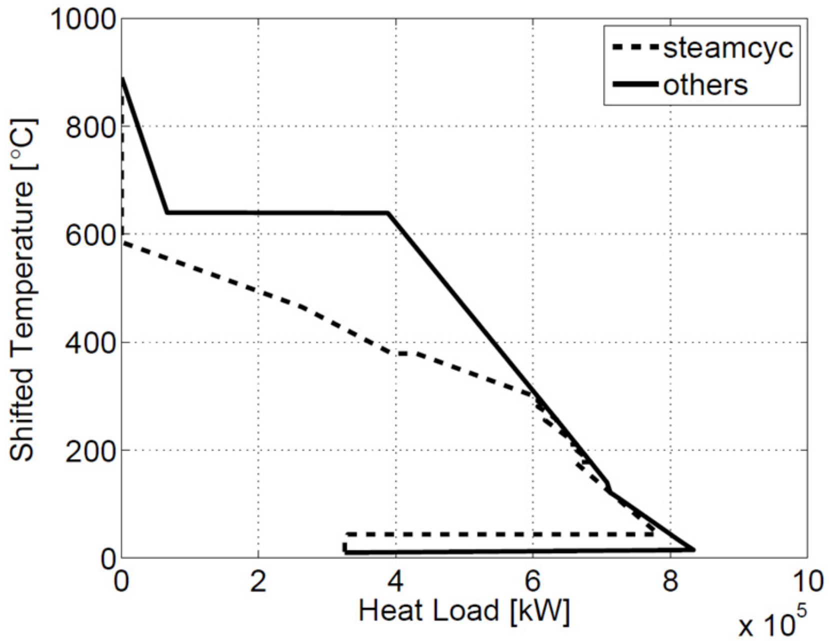


Figure 26: Grand composite curve for the calcium looping process with a steam cycle with reheat (case 1.b)

8.2.3 Integrated steam cycle (case 1.c)

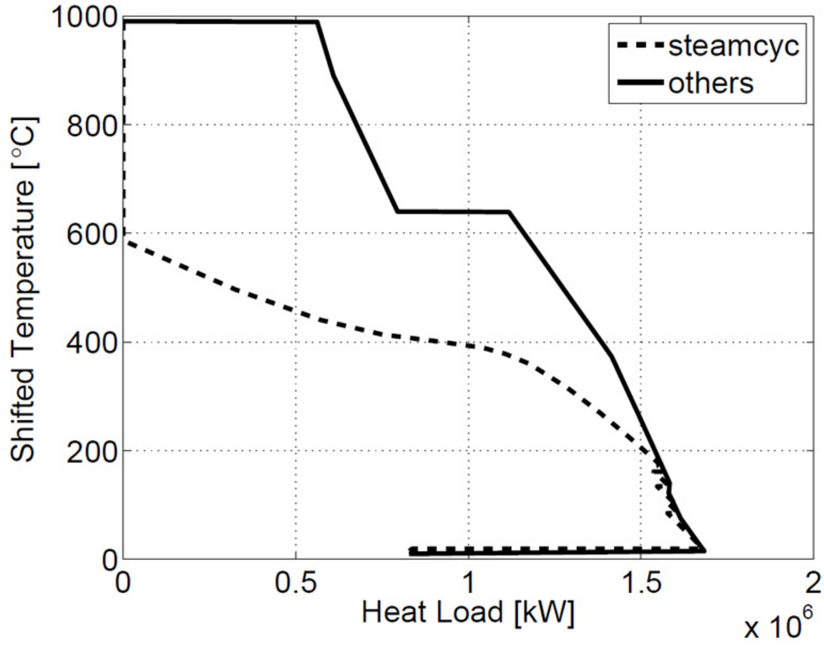


Figure 27: Grand composite curve for coal power plant and calcium looping process integrated in a single steam cycle (case 1.c)

For the case with the coal power plant and the calcium looping process integrated in the same steam cycle we can see the grand composite curve above. The steam cycle is of the same complexity as the reference case, i.e. double reheat and supercritical condition. The background process is now a combination of the (previously separated) coal power plant and calcium looping process, as expected. The area above the steam cycle line and below the background process can be seen to be smaller than for the coal power plant alone, indicating a lower exergy loss than for the reference case.

The main results are summarized in Table 16 below:

Table 16: Integration results for calcium looping and coal power plant to same steam cycle

Results for case 1.c		
Total energy input	1875.2	MW
Total gross output	848.0	MW
Auxiliary electrical consumption (Compression + O_2-separation)	139.0	MW
- Compression	79.5	MW
- O_2-separation	59.6	MW
Total net energy output	708.8	MW
Electrical efficiency	**37.5**	**%**

8.3 Oxy-fuel combustion plant (Case 1.d)

The thermodynamic stream data for the oxy-fuel fired coal power plant are presented in Table 17 below:

Table 17: Stream data for the oxy-fuel plant

Stream	Temperature in [°C]	Temperature out [°C]	Heat load [kW]
Coal plant			
- Radiative heat in boiler	1000	1000	539 989
- Convective heat from flue gas	1000	180	415 316
- O_2 preheating	20	322	111 976
- Heating before flue gas cleaning	340	370	14 104
- Condensation of flue gas	212.4	20	125 577
- Cooling in compression unit	259.9	20	64 942

The result from the oxy-fuel combustion plant integration is shown in the grand composite curve in Figure 28 below. Thermodynamically the major difference between the oxy-fuel fired power plant and the reference plant arises first after the flue gas cleaning, where for the oxy-fuel plant the flue gases are cooled down to 20°C and heat from the compression process is gained. The penalty for using this technology is not shown in the grand composite curve as it arises from the auxiliary energy need used for O_2-separation and compression of the CO_2.

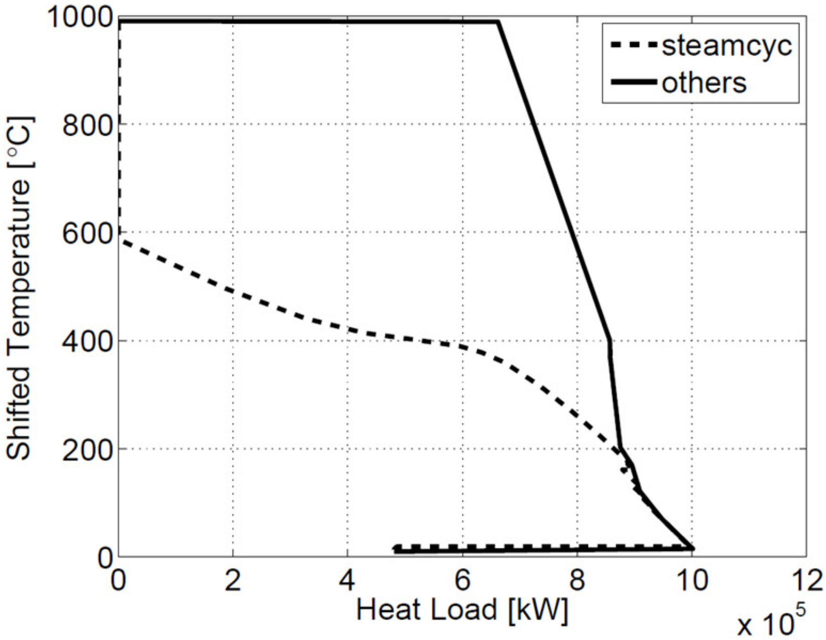


Figure 28: Grand composite curve for oxy-fuel fired coal power plant (case 1.d)

The main results for this case are presented in Table 18 below:

Table 18: Integration results for oxy-fuel fired power plant

Results for case 1.d		
Total energy input	**1042.3**	MW
Total gross output	**492.3**	MW
Auxiliary electrical consumption (Compression + O_2-separation)	**115.3**	MW
- Compression	45.0	MW
- O_2-separation	70.2	MW
Total net energy output	**377.1**	MW
Electrical efficiency	**36.0**	%
CO_2 capture efficiency	**90.4**	%

In theory oxy-fuel technology should capture 100% of the CO_2 produced in the power plant, however according to Rubin et al. (2007) the theoretic 100% capture efficiency only holds under ideal conditions and various studies have placed the actual capture efficiency at 90-98%. Rubin et al. also made their case study in the same publication under the assumption that the capture efficiency for oxy-fuel would be at 90% which is similar to the results obtained above. The CO_2 that is not captured in this model is washed away with the purged water in the flash tanks before and under the compression section.

8.4 Comparison of electrical efficiency for coal power plant with calcium looping

When calcium looping is used as a post-combustion carbon capture in a coal power plant an efficiency penalty is introduced is introduced due to the fact that more coal is used in the plant and extra energy demand is introduced due to the need for air separation and compression of carbon dioxide. In all of the configurations that were investigated the coal consumption for the main coal power plant was kept constant and the extra coal for the calcium looping process was also constant between the three cases of calcium looping integration since the carbon dioxide production is constant. The differences are therefore only related to different arrangement of the heat recovery section for steam generation and layout and steam values of the suggested steam cycles.

A breakdown of the gross power output for all of the cases is presented in Figure 29 below, where the gross output is the sum of the net energy output and the internal consumption (in this case meant the additional internal consumption in form of O_2 separation and CO_2 compression):

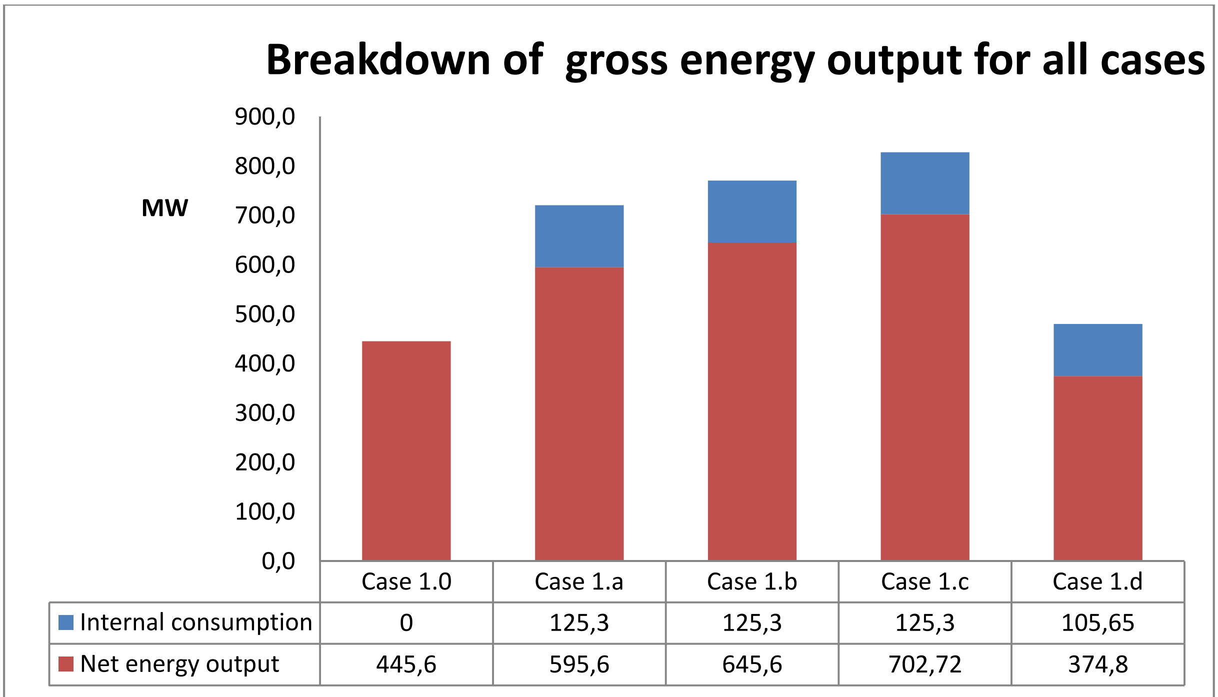
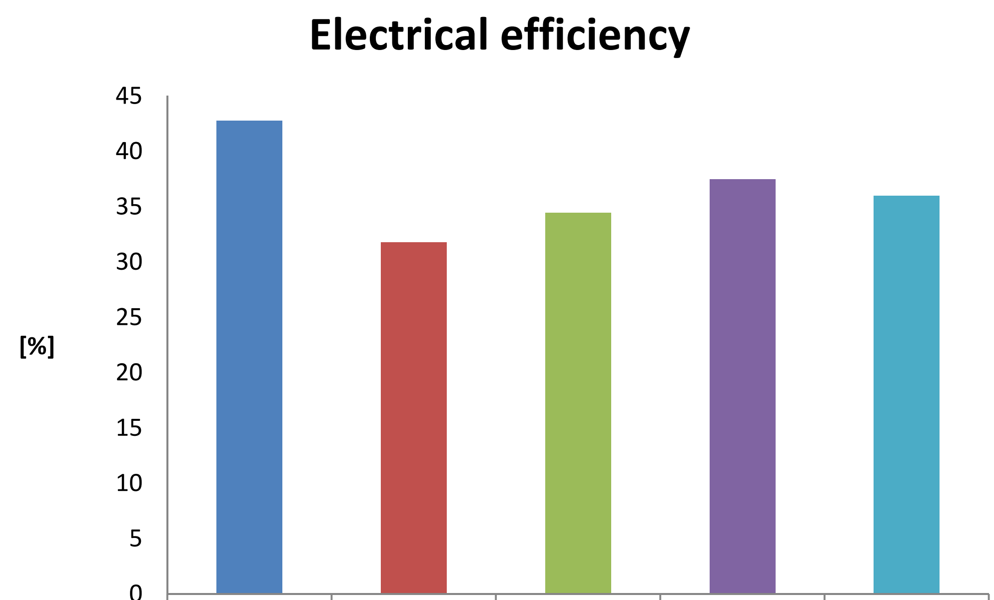


Figure 29: Breakdown of the gross energy output for all cases, divided into net energy output and internal consumption specific to addition of carbon capture

As can be seen in the diagram above, the total energy output for the 3 cases of calcium looping is higher than for case 1.0 and 1.d. This is due to the higher total energy input (in the form of coal) in these cases, which is needed for the regeneration of the limestone. The total energy input for the calcium looping cases are 1875.2 MW, while the total energy input is 1042.3 MW for the cases 1.0 and 1.d.

For all these configurations that have been presented, the thermal efficiencies of the plants are presented in Figure 30 below:



	Case 1.0	Case 1.a	Case 1.b	Case 1.c	Case 1.d
Efficiency	42,8	31,8	34,4	37,5	36,0

Figure 30: Comparison of electrical efficiency between different configurations compared to the reference plant and oxy-fuel plant

As shown in the diagram above, the alternative with two separate steam cycles for the calcium looping and the coal power plant (i.e. cases 1.a &1.b) are the ones that introduces the largest penalty to the efficiency of the plant. This is due to loss of potential heat recovery when using a separate and less efficient steam cycle (which is used for the calcium looping process). Even if case 1.b results in less of a penalty than case 1.a due to utilizing a reheat of the steam after the first turbine stage, it is still not as good as using oxy-fuel technology as is done in case 1.d, making oxy-fuel technology preferable unless existing steam cycle allows for integration of calcium looping as done in case 1.c.

The integration of one steam cycle with the coal power plant and the calcium looping process (case 1.c) results in the highest electrical efficiency for the total process among the analysed carbon capture configurations with a 5.3%-points penalty compared to the base case 1.0. This All of the penalties are in line with the expected values for the efficiency penalty as a result of integrating calcium looping technology with a coal power plant (as discussed in chapter 5.4), with case 1.c coming close to the lowest reported possible efficiency penalty.

8.4.1 Calcium looping as a post-combustion capture process

The results of the integration of calcium looping presented above indicate that the impact of carbon capture on the plant electrical efficiency can vary considerably depending on how the integration is set up and the complexity of the steam cycle, as can be seen when comparing between the different cases and their individual results. While it is clear that that a more advanced steam cycle would result in higher efficiency, this work was conducted to investigate maximum efficiency levels of suggested processes. In addition, by varying the complexity of the steam cycle layout it was possible to estimate the room for efficiency improvement. This in fact does not depend only on the steam cycle itself, but on the temperature-heat load profiles of the combustion processes and other possible heat sources and heat sinks. Even if pricing information is not readily available one can make the assumption that a 0.1% increase in efficiency might not justify building a steam cycle which is substantially more complex (and thus more expensive) for example. According to our investigation however the efficiency increase gained from building a steam cycle with reheat of the steam resulted in an almost 3% increase in efficiency, which is a respectable increase in efficiency and should be recommended.

The optimal configuration of implementing calcium looping in a coal power plant (which should ideally be the configuration of choice if calcium looping should be implemented as proposed in tis thesis) is the case where the calcium looping process and the coal power plant share the same steam cycle (case 1.c), or alternatively put, where the calcium looping process is “hooked-up” to the advanced steam cycle of the coal power plant. This should not surprise, as making all the thermal streams available for one steam cycle should open up for more integration options than the case in which coal power plant and calcium looping are integrated to separate steam cycles. The latter however is probably the most viable solution when the coal power plant is already in place and the calcium looping is considered as a successive plant upgrading. Other reasons for choosing the option of having two separate steam cycles can be spatial restrictions or size of investment costs if there is already an existing steam cycle that has none or small expansion capacity (thus making it necessary to replace it completely if wishing to integrate everything into one steam cycle).

If the single steam cycle integration is not possible to implement or not desired for some other reasons then oxy-fuel coal combustion and subsequent water separation appears the more efficient alternative for carbon capture. Oxy-fuel may also be the cheapest alternative from an investment point of view as no new steam cycle is built, leaving only the air separation unit and the CO_2 compression equipment (which is needed for all investigated cases in this thesis).

It must also be noted that in theory there is a difference in potential of CO_2 capture between the calcium looping technology and the oxy-fuel technology. The calcium looping is in this thesis designed to achieve 90% capture efficiency whereas the oxy-fuel combustion technology should in theory be able to capture all produced CO_2, however the efficiency measured in the modelling of our thesis was 90.4%, as shown in Table 18. Thus, any eventual monetary gains from CO_2 emission avoidance by using oxy-fuel technology over calcium looping may not necessarily have to be much larger at all.

As the objective of this thesis was primarily to investigate the impact on electrical efficiency of implementing calcium looping technology no economic comparisons have been made beyond cost of avoidance data per avoided ton of CO_2 from literature. As none of the configurations of calcium looping integration differ in amount of avoided CO_2 emissions that data might not have been the most relevant, but investment costs for steam cycles (turbines, heat exchangers, piping etc.) might differ more and would be an interesting aspect to consider in a future study of calcium looping technology.

Another interesting aspect in terms of economic comparison is the comparison in regards to other capture technologies (which may admittedly be more difficult to estimate). According to literature calcium looping has a relatively low cost of avoidance of CO_2, one of the two lowest of the ones compared in this thesis, and thus it has a competitive edge towards the other technologies for post-combustion carbon capture. This is particularly so as the literature states that the investment cost for all technologies lie in similar ranges, thus making the avoidance cost a very interesting variable.

An additional point to take into account for the economics of the calcium looping technology would be the economic value on the purged sorbent (CaO) (if no direct integration with cement plant or similar process is either possible and/or desired). This potential source of income may improve the economic balance of investing in calcium looping technology, especially in case the costs for emitting CO_2 are high, as such a large portion of CO_2 emissions in cement plants come from calcination (as has been previously stated).

8.5 Cement plant integration

In this chapter the composite curves of the cement plant in different combinations with calcium looping and the reference power plant are shown.

In addition to the combination of power plant and calcium looping the integration of a cement plant into that system and accordingly the changes caused by this combination in the cement production line are investigated. Thus the power production of the power plant and the cement production of the cement plant are not altered but stay the same as in the single base cases of both plants. The power generation of the whole system consisting of power plant, calcium looping and cement plant is maximized.. The investigation of cement plant combined with power plant and calcium looping process are conducted and presented in the corresponding paragraphs.

The three investigated cases are:

1. the base case cement plant (2.0),
2. the base case cement plant in combination with a power plant and a calcium looping process (2.a)
3. and a limestone free cement plant in combination with a power plant and a calcium looping process (2.b).

The heat integration of the three cases is investigated and presented in this order.

8.5.1 Base case cement plant (case 2.0)

There are three thermal streams that are relevant for heat recovery in the base case cement plant. These streams are shown for the base case configuration with the mass flow, temperature levels and their head load in Table 19.

Table 19: Heat load data of the base case cement plant

Stream	Temperature in [°C]	Temperature out [°C]	Heat load [kW]
Feed preheater	10	700	36460
Flue gas cooler	950	150	57769
Hot Air cooler	1100	50	693

Figure 31 shows the composite curve of the cement plant with the potential of integration into a steam cycle. The integration into a steam cycle can be reasonable but is depend on the individual case due to low thermal energy exchange between its material streams compared to the reference power plant – especially in combination with the calcium looping; nevertheless it is already high enough that it can be reasonable to use this energy in a small steam turbine. This decision is depending on the specific case, on the detailed operation data of the plant and the intention of its operator. In this case the sizes of the combined plants play a role. Whereas the power plant is large, the cement plant is of a conventional size.

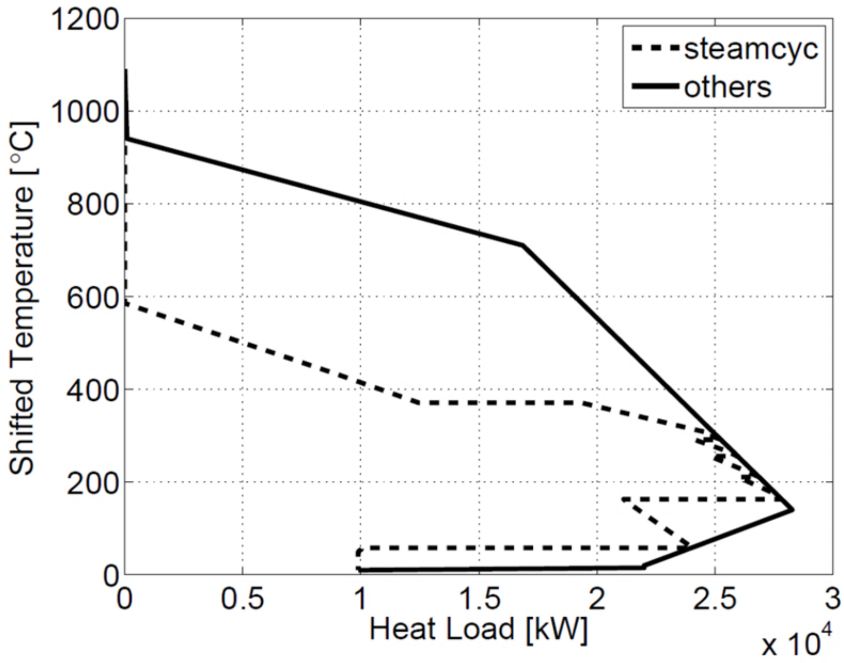


Figure 31: Composite curve of reference cement plant

8.5.2 Combinations of cement plant and power plant with calcium looping

The heat integration of the base case cement plant in connection with the base case power plant and a calcium looping process for capturing the carbon dioxide produced in the two plants is discussed here. The heat load of the raw material stream compared to case 2.0 (base case cement plant) changes due to changed mass flow rates. The mass flows needed to be adjusted since the raw material stream in the cement plant is reduced about the amount of spent sorbent/purge that is injected into the kiln as well. This purge is not cooled down anymore as in case 2.0 but gets preheated to 950°C so it enters the kiln at the same temperature as the raw material stream. This leads to changes in the flue gas composition of the flue gases from the kiln which again influences the flue gas composition of the calciner due to the circulation of flue gases. The exhaust gas going to the calcium looping process has a lower mass and volume flow due to the reduced amount of coal and air in the combustion and is reduced about a significant amount of CO_2 due to the replacement of limestone by lime (purge). This again leads to a scaling of the calcium looping process and a higher amount of supplementary coal firing. The scaling of the calcium looping is necessary as a higher amount of flue gases compared to case 1.c needs to be treated and is represented in the model by the rising amount of the supplementary firing and the additional fresh limestone make up.

The new heat load data can be found for the combination of the reference cement plant with the coal power plant and the calcium looping in Table 20 and for the limestone free cement plant with the coal power plant and the calcium looping in table 21.

The composite curves are presented in Figure 32 and Figure 33 respectively.

To highlight the effect of additional power generation obtained by recovering the heat available from the cement plant for steam generation the pictures contain in red the non-integrated version and in black the integrated version.

8.5.2.1 Cement plant with coal power plant and calcium looping process (case 2.a)

Figure 32 is showing the curves of the base case cement plant and the reference power plant with calcium looping. The calcium looping is used for the CO_2 capture of the power plant as well as of the cement plant. Therefore the heat loads involved in the cooling and heating processes are larger compared to case where the calcium looping process is used only for capturing the carbon released by the coal power plant due to the increased CO_2 flow and correspondingly the increased $CaCO_3$ and coal flow.

Table 20: Heat load data of the base case cement plant in combination with a power plant and calcium looping process

Stream	Temperature in [°C]	Temperature out [°C]	Heat load [kW]
Feed preheater	10	700	21033
Flue gas cooler	950	150	41171
Hot Air cooler	1100	50	11416
Carbonator	650	649	396974
CO_2 cooler	900	20	275703
CO_2 lean flue gas cooler	650	150	198322
O_2 preheating	15	100	6478
Purge preheating	650	950	4954
Intercooling compression	259	20	139544

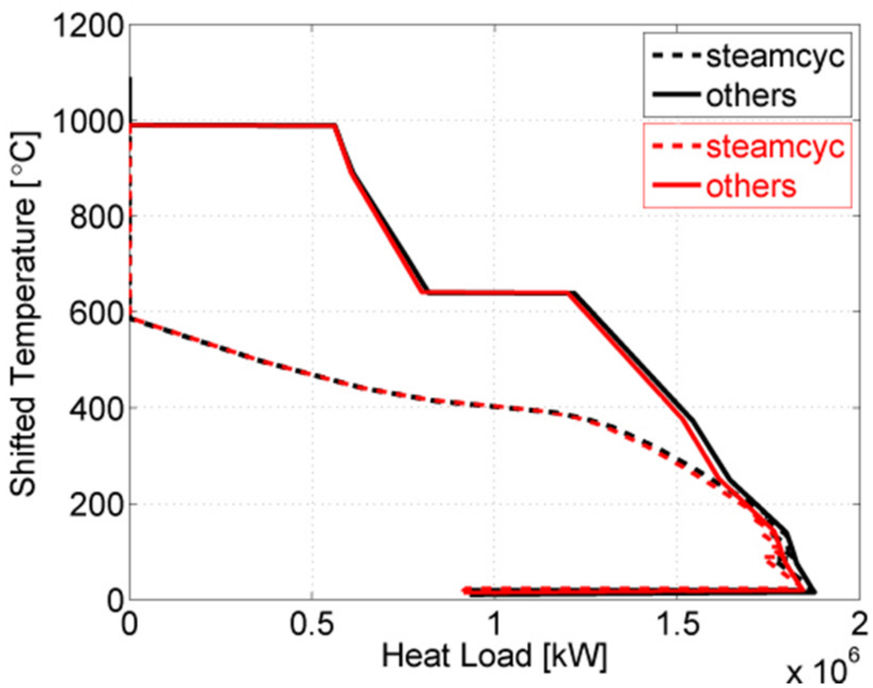


Figure 32: Composite curve of case 2.a; black completely integrated into steam cycle, red only power plant and calcium looping integrated into steam cycle

Limestone free cement plant with coal power plant and calcium looping process (case2.b)The difference between integration of the available heat of the cement plant into a steam cycle with coal power plant and calcium looping process or only the integration of coal power plant and calcium looping process cannot be seen any more at this level of detail. The available additional heat load of the cement plant is very small.

Table 21: Heat load data of a limestone free cement plant in combination with a power plant and calcium looping process

Stream	Temperature in [°C]	Temperature out [°C]	Heat load [kW]
Feed preheater	10	700	15969
Flue gas cooler	950	150	17709
Hot Air cooler	1100	50	14240
Carbonator	650	649	335056
CO_2 cooler	900	20	241743
CO_2 lean flue gas cooler	650	150	186398
O_2 preheating	15	100	5695
Purge preheating	650	950	5510
Intercooling compression	259	20	122246

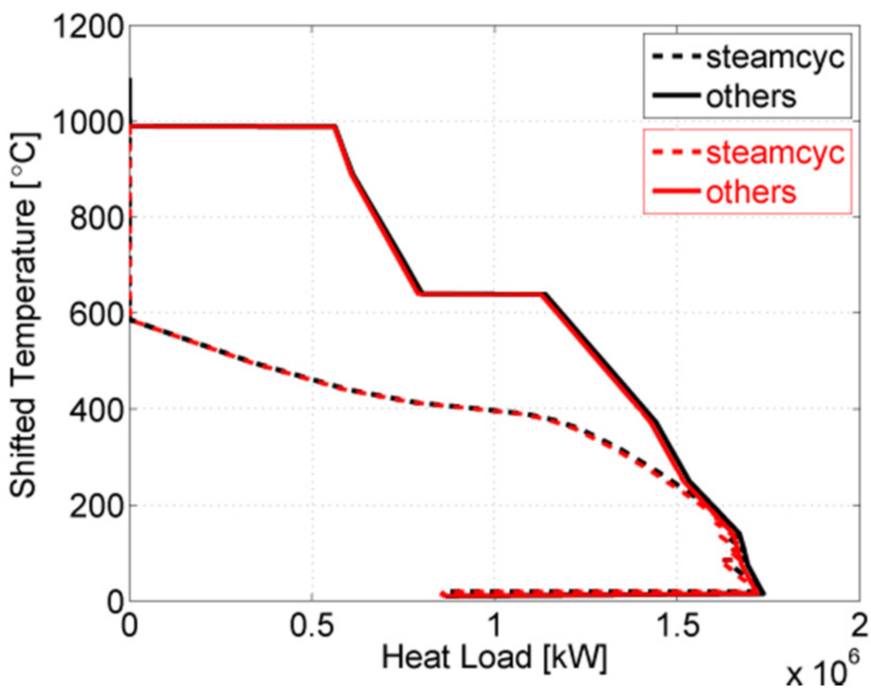


Figure 33: Composite curve of case 2.b; black completely integrated into steam cycle, red only power plant and calcium looping integrated into steam cycle

The difference between the fully integrated black curve and the red curve where only the power plant and the calcium looping are taken into account is very little as the major raise in the energy production happens in the calcium looping, whereas the cement plant delivers only around 1 – 2% of the total energy amount to the steam cycle.

Table 22: Results of the thermal integration of the cement plant to the coal plant with calcium looping

Base case cement plant with power plant and calcium looping (case 2.a)		
Total energy input	2106.9	MW
- Energy input for coal plant	1042.3	MW
- Energy input for calcium looping	984.9	MW
- Energy input for cement plant	79.8	MW
Auxiliary electrical consumption (Compression + O_2-separation)	154.4	MW
- Compression	80.6	MW
- O_2-separation	70.1	MW
Gross energy output	909.7	MW
Net energy output	759.0	MW
Total electrical efficiency	**36.0**	**%**
Limestone free cement plant with power plant and calcium looping (case 2.b)		
Total energy input	1925.2	MW
- Energy input for coal plant	1042.3	MW
- Energy input for calcium looping	861.1	MW
- Energy input for cement plant	21.9	MW
Auxiliary electrical consumption (Compression + O_2-separation)	132.4	MW
- Compression	70.8	MW
- O_2-separation	61.6	MW
Gross energy output	851.0	MW
Net energy output	718.6	MW
Total electrical efficiency	**37.3**	**%**

8.5.3 Comparisons of the cement plant cases

The impacts off the cement plant will be measured for the cases 2.0, 2.a and 2.b by the extra effort for the clinker production in addition to the effort for case 1.c and compared to that case regarding the additional specific changes in energy input via coal combustion, CO_2 emission, limestone consumption, power production and the scaling factor of the calcium looping process.

The results presented in this chapter show significant changes in the additional specific energy demand, the additional specific CO_2 emission, additional specific limestone demand and electricity output for the cement plant with integration into a shared calcium looping process with a power plant. The additional specific energy demand is double for case 2.a whereas it drops slightly for case 2.b (limestone free cement plant). The additional specific CO_2 emission and additional specific limestone demand decrease significantly for the integrated study cases 2.a and 2.b compared to 2.0 and the electricity output rises for the cases where the cement plant is integrated into the steam cycle of the power plant and calcium looping as for the case without a use of energy only produced in the cement plant. The size for these changes is shown in 8.5.3.4 where the scaling factor for the calcium looping is presented. The results of the efficiency increase of the whole system for electricity generation as well as the aforementioned results support the integration of the power plant with the cement plant.

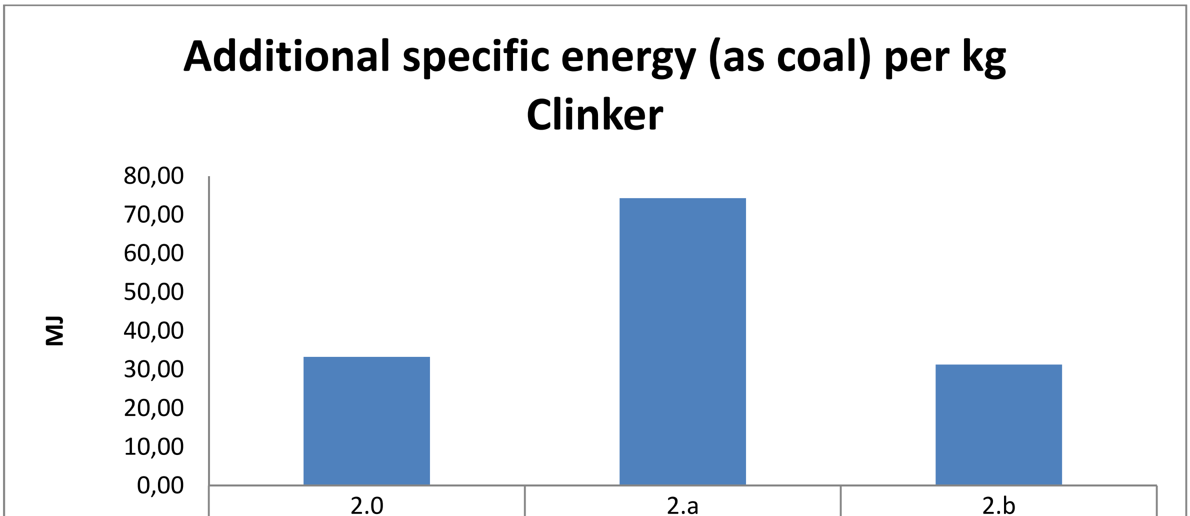
In detail these benefits result from different contributions which are presented and discussed in the following paragraphs.

8.5.3.1 Coal input

Due to the different coals used in the simulations the comparison of fuel demand will be presented in MJ/kg clinker.

The energy demand in this case is defined to be the energy of the fuel used in the combustion processes. These combustion processes that occur are located in the power plant (coal combustion for steam generation), in the calcium looping (supplementary coal combustion in calciner) and in the cement plant (combustion in calciner and kiln). All of these coal flows are converted into energy flows in MJ and added.

The basic energy demand is defined as the energy of fuel used in the combustion processes of case 1.c. The additional energy demand is defined as the difference between the total energy demand and the basic energy demand. This additional energy demand is calculated in MJ per kg of clinker – the desired product of the cement plant. The diagram Figure 34 shows how the additional energy demand varies with the different configuration options for the cement plant.



	2.0	2.a	2.b
MJ/kg Clinker	33,27	74,27	31,26

Figure 34: Specific additional energy demand for different study cases

It can be seen that the additional specific energy demand is highest for the cement plant with power plant and calcium looping and gets reduced over case 2.0 to 2.b. The addition coal consumption of the limestone free cement plant (2.b) is slightly lower than the integrated base case cement plant (2.a).

The additional specific energy demand consists of the parts for the heat generation in the calcium looping due to a higher heat demand in the calciner and for the calciner and kiln in the cement plant. The additional specific energy demand is depending on the mass flow rates in the devices. Thus, to heat up a mass flow its reduction leads to a lower energy demand and correspondingly a rising mass flow to higher energy demand. The connection of the cement plant with the calcium looping process and the power plant leads to changing mass flows in the feed stream in the cement plant and therefore in the flue gas which is redirected to the calcium looping so as to the circulating mass flow rates for flue gas and respectively the solid streams change as well. The benefits (as mentioned in chapter 7.2.4) of this connection are the usage of the purge of the calcium looping process in the cement production and replacing a part of the raw limestone.

The additional specific energy demand of case 2.0 (33.27 MJ/kg clinker) doubles for case 2.a. The reason can be found in the calcium looping. While the energy demand in the cement plant itself drops, the energy demand in the calcium looping increases. The drop and the raise are not even, the drop in the cement plant is a higher in percentage – 26% compared to 18% raise in the calcium looping – but smaller in total numbers – 28 MW in the cement plant compared to 152 MW in the calcium looping.

The lowest additional energy demand is achieved with a limestone free cement plant that uses exactly the amount of CaO that is taken out of the calcium looping in the purge. Here no calciner in the cement plant is necessary and the amount of circulating flue gases in the calcium looping is not increasing significantly. Therefore the energy demand in the cement plant drops drastically (80%, 86 MW) and the energy demand in the calcium looping rises only slightly (3%, 28 MW).

8.5.3.2 Additional and total electricity output

Besides the above described effects the electricity output for the different study cases varies as well. As shown in Figure 35, the base case cement plant (2.0) produces 10 MW of electricity whereas the electricity production for case 2.a and all components integrated into one steam cycle raises about 62 MW.

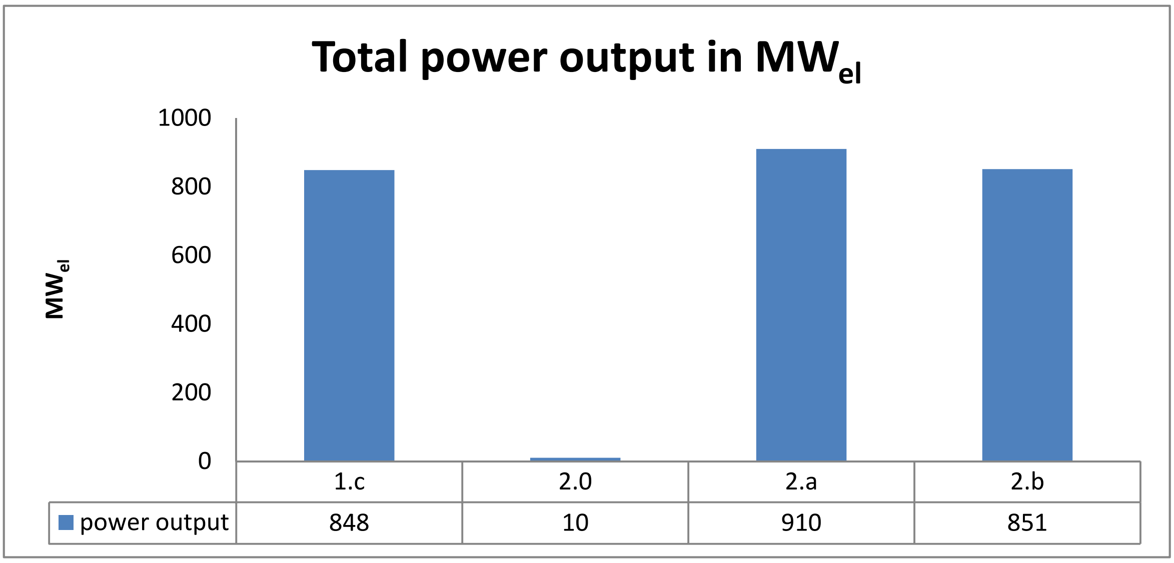


Figure 35: Total electricity output for different study cases

This leads to the conclusion that the major part of this additional electricity, 52 MW, is produced in the adjusted calcium looping process. For case 2.b the major energy delivery will also occur in the calcium looping process, as the thermal streams of the cement plant (see Table 21) are significantly smaller than in case 2.0 (see Table 19).

The additional power production results from the additional heat load of the streams mainly caused by the higher amount of circulating flue gases in the calcium looping. The mass flow rates in the heaters and coolers define together with the temperature levels the head loads of the streams. Therefore a higher heat transfer to the steam cycle is possible. .

The rising energy output has basically two reasons:

1. The base case cement plant can be integrated into a steam cycle and produce electricity (see Figure 35, column 2).
2. The calcium looping process produces more energy as the supplementary coal firing rises with increasing amount of flue gases.

Considering that the main part of energy generation is done in case 1.c in the following paragraph the results for the additional specific electricity output per kg produced clinker is presented.

The basic electricity output is defined as the electricity output of the above mentioned case 1.c, whereas the additional output is the total produced amount of electricity in the respectively case minus the basic electricity output. The additional electricity output is converted into the additional specific electricity output to achieve a better comparability between all study cases.

$$P_{base} = P_{out_{1.c}} \tag{7}$$

$$P_{add_{2.a}} = P_{out_{2.a}} - P_{base} \tag{8}$$

Figure 36 shows the additional specific electricity output. It can be seen that case 2.0 has the lowest additional specific electricity output as it cannot benefit of a calcium looping cycle with an electricity generation 6 times as high as the cement plant. These benefits can clearly be seen in case 2.b.

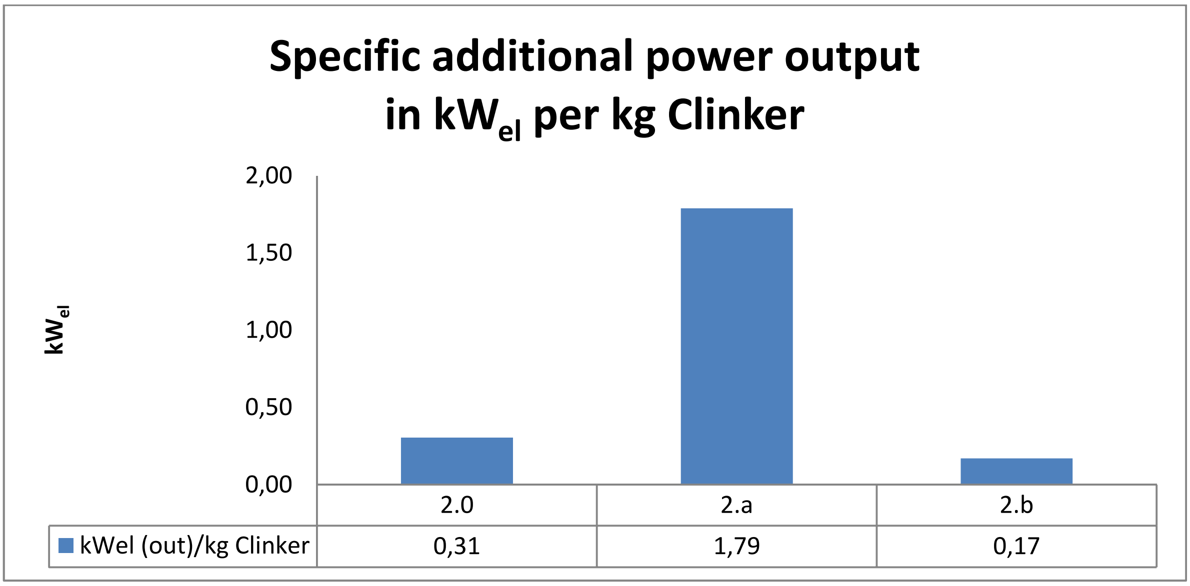


Figure 36: Specific additional electricity output for different study cases

The results presented in Figure 35 and Figure 36 proves that the major part of the additional electricity production happens in the calcium looping process. The reason is found in the proportion of the coal consumption in the processes and therefore the head loads of the different streams as presented in chapter 8.5.2.

This is underlined by the composite curves of the integration of the base case cement plant and the limestone free cement plant in Figure 32 and Figure 33. The curves of the fully integrated case (black) and the case without integration (red) of case 2.a and 2.b differ only about the amount of heat delivered by the cement plant which is compared to the heat delivery of case 1.c very small (around 1 – 2%).

8.5.3.3 Electric efficiency

Under the assumption that the whole system consisting of power plant, calcium looping process and cement plant is only used for the power generation – cement is considered as a by-product – an electric efficiency can be calculated. The total power output will be affected by the inclusion of the cement plant (by the addition of more flue gases in the calcium looping process) and the energy input in form of coal will also increase. The electric efficiency for the whole plant (coal power plant, calcium looping process and cement plant as one unit) is defined as in equation 9 below:

$$\eta_{el} = \frac{W_{tot}}{(Q_{power\ plant}+Q_{CaL}+Q_{cement})} \tag{9}$$

This is necessary to receive a number for the efficiency penalty due to the inclusion of the cement plant. Those numbers for cases 2.0, 2.a and 2.b can be found in Figure 37 compared to the cases 1.0, 1.c and 1.d.

It can be seen, that case 2.a has the same electric efficiency as case 1.d (oxy-fuel plant) and case 2.b (limestone free) approximately the same as 1.c. The efficiency penalty for a slightly higher power production in the combination of all three processes is very small – 1.5

percentage points for the base case cement plant and 0.2 percentage points for the limestone free cement plant – compared to 1.c and the overall efficiency penalty to the reference power plant ranges from 5.5 to 6.8 percentage points, which is as mentioned in chapter 5.4 a low efficiency penalty for calcium looping.

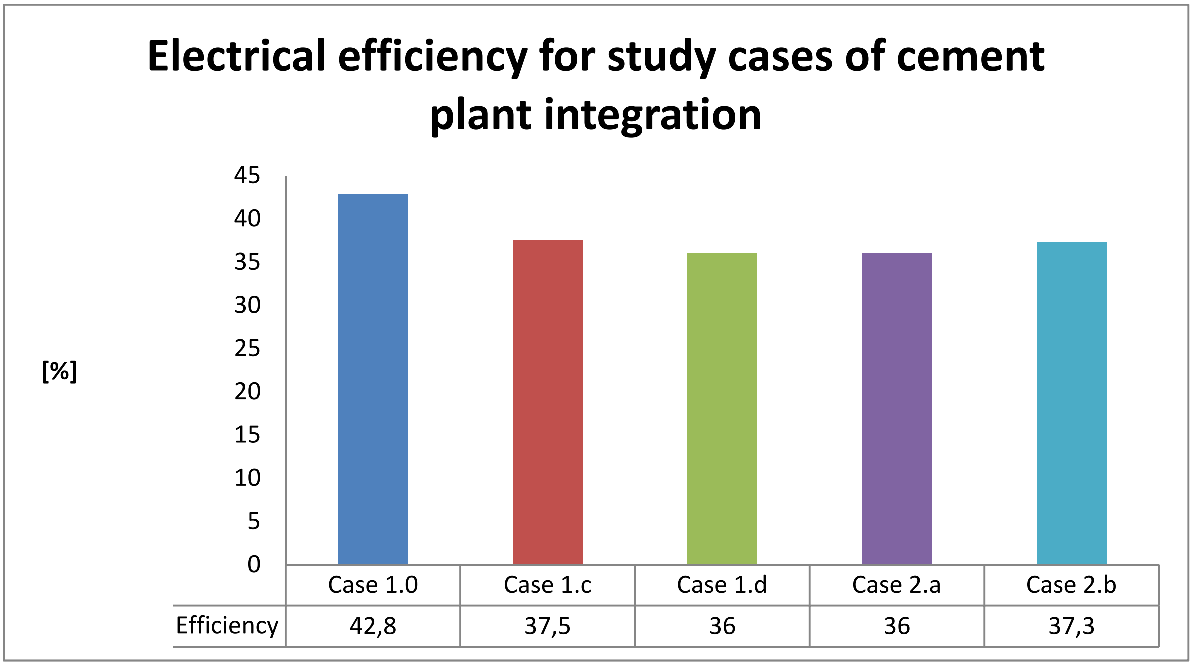


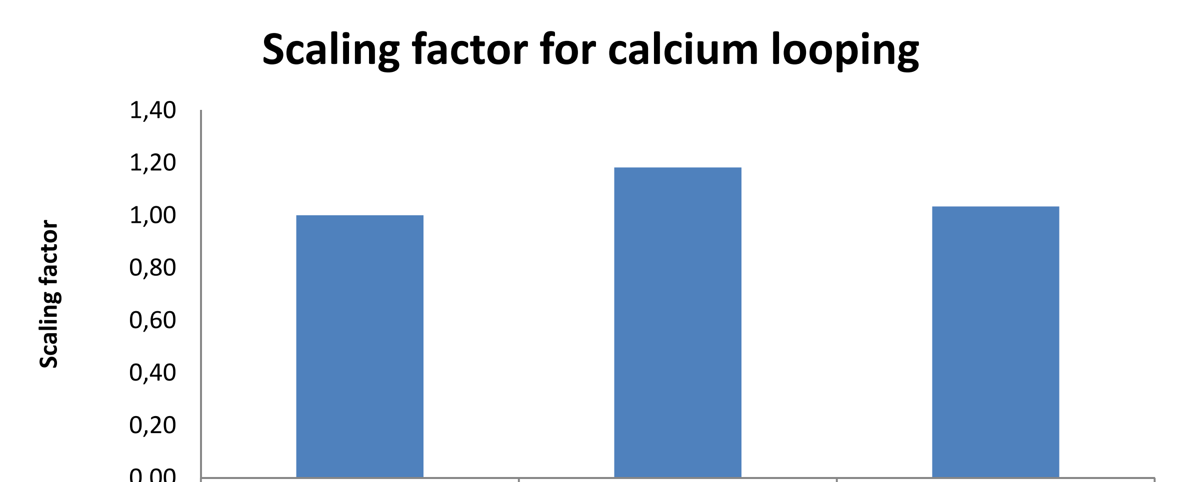
Figure 37: Comparison of electric efficiency for the two cases of cement integration versus the reference plant and best alternative of CaL integration as well as oxy-fuel case

The presented results of the electric energy of the study cases of power plant, calcium looping and cement plants show that this combination of coal power plant and cement plant with the calcium looping technology is very interesting. On the one hand the efficiency penalty is low with a range of 0.2 to 1.5 percentage points and even in worst case competitive to an oxy-fuel power plant and other CCS technologies; on the other hand there is a second sellable product: the cement.

These results can be explained in the fact that a huge part of the additional energy demand in form of coal can be used as heat supply for a steam cycle for electricity generation. The losses are found in the electric efficiency penalty.

8.5.3.4 Scaling factor of calcium looping process

While the power plant configuration is not changed for the integration of the cement plant into cases 2.a and 2.b the calcium looping process needs to be adjusted according to the new flue gas volume that needs to be separated into a CO_2 rich and lean flue gas stream. For a comparison of the sizes a scaling factor – shown in Figure 38 – has been calculated according to the consumption of supplementary coal in the regenerator in the calcium looping process. The scaling factor for the basic study case is set to be 1 and provides a reference for calculating the scaling factor of the calcium looping in the other configurations. The scaling factor of the calcium looping process is interesting for the evaluation of the benefits – such as low additional specific energy consumption, reduction of CO_2 emission and reduction in limestone consumption – of cases 2.a and 2.b.



	1.c	2.a	2.b
Scaling factor	1,00	1,18	1,03

Figure 38: Scaling factor of the calcium looping process for different study cases

The scaling factor includes the whole scaling of the calcium looping process of the reference power plant if integrated with a cement plant. The number in the results show that the scaling of the calcium looping is comparably small, even with the reference cement plant which is a conventional size the scaling of the calcium looping is only +18% to case 2.a. The scaling factor for case 2.b is only +3% which means that the cement production is nearly for free since the limestone can be completely replace by a reduction of the clinker production about only 50%.

8.5.3.5 Limestone mass flow

Besides the CO_2 emission another important point to create a more sustainable and less expensive clinker production line is the reduction of raw material intake. The calcium looping process uses a lot of limestone and produces a purge flow with deactivated lime that cannot be carbonated anymore but is still useful in the cement production. This lime purge from the calcium looping can therefore be used to replace the limestone flow needed in the cement plant. To show this effect, the total mass flow rate of limestone in the whole system (Figure 39) and the additional limestone demand per kg clinker (Figure 40) are presented.

The total mass flow rate of limestone in Figure 39 shows that the difference in limestone demand for study case 2.0 and 2.a is very small. Therefore the use of the raw material limestone stays approximately constant for process integration for CO_2 capture. A similar result is shown for case 1.c and 2.b: Here the demand of limestone differs considerably as well, the calcium looping uses the part of limestone the cement plant (half of the size of the base case plant). The raw material for the cement plant is already pre-processed in the calcium looping and nearly no extra demand is left.

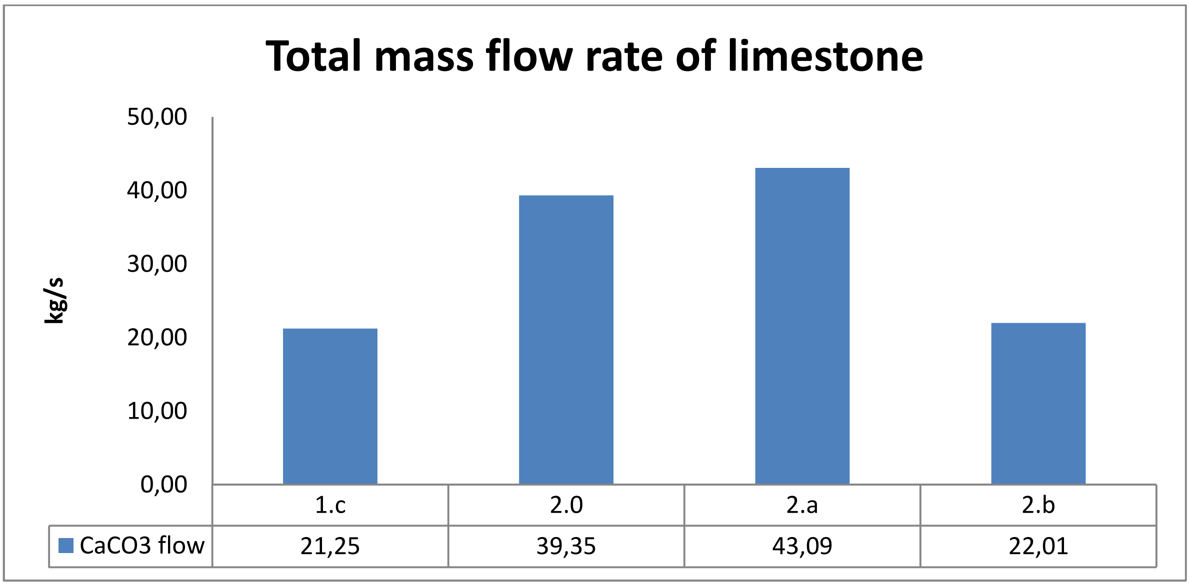


Figure 39: Total mass flow rate of limestone for different study cases

The comparison for the additional specific limestone demand clarifies these results.

The basic limestone demand is defined as the limestone demand for case 1.c. The basic limestone demand is constant for all cases as the configuration for the power plant and the calcium looping is not changed.

The additional limestone demand is defined as the total demand of limestone in the study case minus the basic demand of limestone.

$$\dot{m}_{limestone_{base}} = \dot{m}_{limestone_{1.c}} \tag{9}$$

$$\dot{m}_{limestone_{add}} = \dot{m}_{limestone_{2.a}} - \dot{m}_{limestone_{base}} \tag{10}$$

Besides the changes in the limestone demand in the cement plant, the limestone demand changes in the calcium looping process as well due to a variation of flue gasses and therefore a variation in the amount of CO_2 that needs to be captured. All these variation are detected in the additional limestone demand.

It can be seen from Figure 40 that the reduction potential of the additional specific limestone demand for the clinker production is quite large. Already a connection with a power plant and a calcium looping process and replacing a part of the limestone reduces the specific demand about 50% whereas case 2.b (limestone free cement plant) without an own raw material limestone flow reduces the additional specific demand about 97%.

The additional limestone consumption results from the limestone consumption in the cement plant and the rising consumption in the calcium looping due to a bigger amount of circulating flue gases.

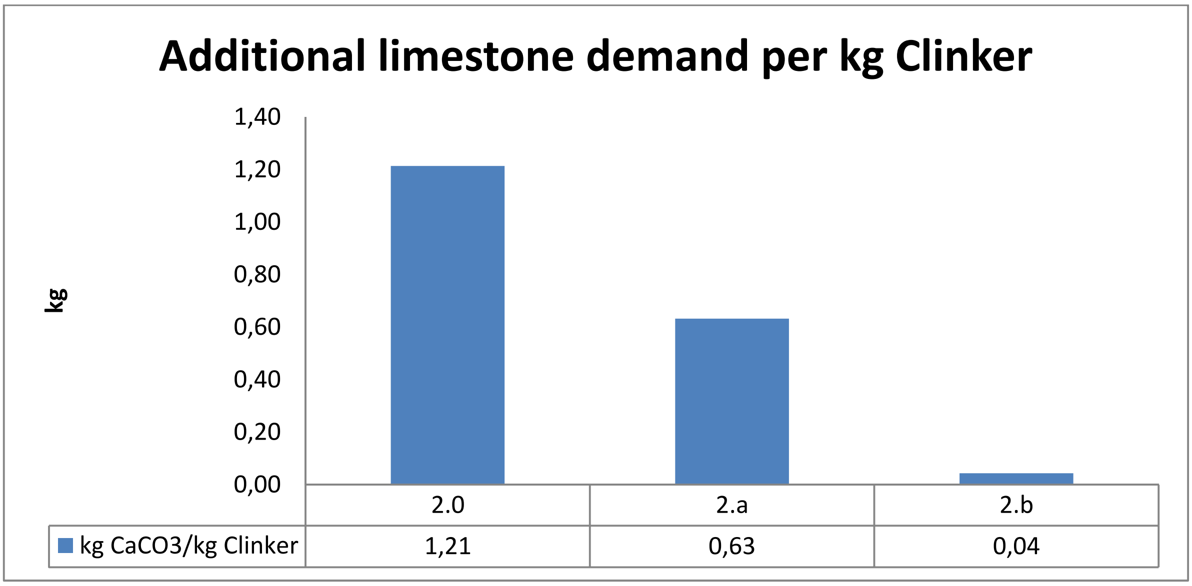


Figure 40: Specific additional CaCO3 demand for different study cases

The limestone consumption differs only in a very small range for the integration of cement plant with calcium looping and power plant in all comparable study cases. This is due to the fact that the purge of the calcium looping process can be used for the cement production and only a small amount for the raised flue gas mass flow need to be added.

8.5.3.6 CO_2 emission

In the following paragraph the specific CO_2 emissions are calculated and compared in order to evaluate the CO_2 saving potential.

The basic CO_2 emissions are defined as the CO_2 emissions released by power plant and calcium looping in case 1.c. The additional CO_2 emissions are defined as the CO_2 emissions released in the respective study case (2.a and 2.b) minus the basic CO_2 emissions. The only exception is study case 2.0 since it is operating without a power plant and therefore the basic CO_2 emissions are zero, only additional CO_2 emissions are shown. The additional CO_2 emissions are converted into additional specific CO_2 emission per kg clinker and in Figure 41 these specific emissions are shown for the study cases 2.0, 2.a and 2.b.

The additional specific CO_2 emission (Figure 41) result from the combustion of the additional coal consumption (shown in this thesis as additional energy demand) in the cement plant and calcium looping as well as in the released CO_2 of the conversion of limestone into lime.

As expected, case 2.0 has the highest additional specific CO_2 emissions as all CO_2 release in the cement plant is released to the atmosphere. The CO_2 emissions in case 2.a drop due to the capture efficiency of 90% in the calcium looping and due to the reduction of raw material and additional energy demand. In this way a reduction potential in the CO_2 emission of more than 97% can be reached as seen in case 2.b. Due to the raising replacement of raw material and the dropping demand of additional energy (less coal in calciner needed) the CO_2 emission for the cement production reach their minimum in this study case, whereas case 2.b has a reduction potential of 94%.

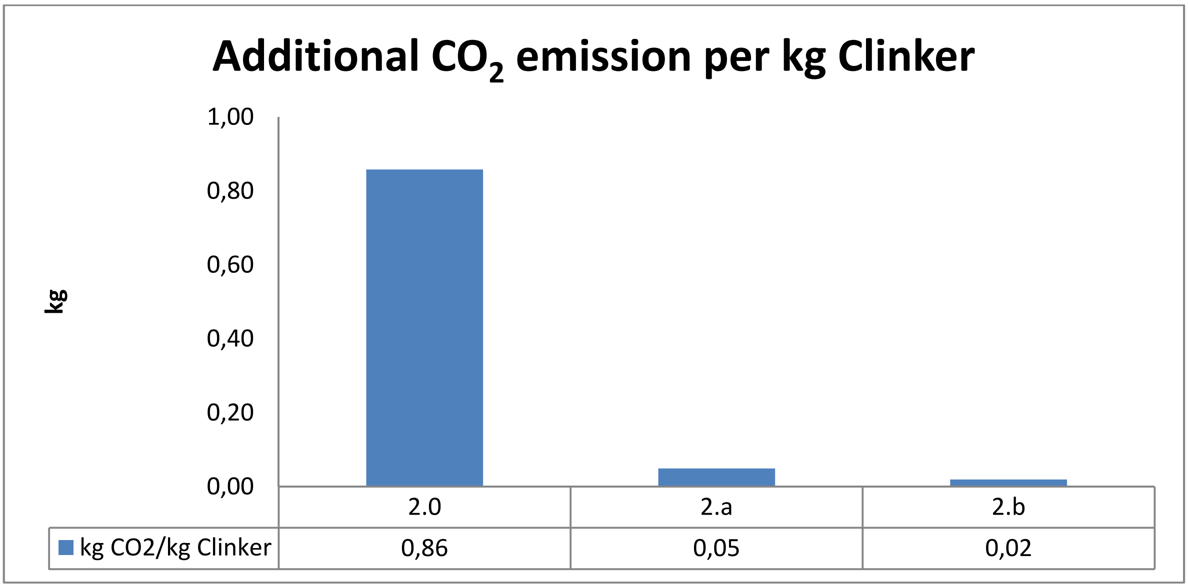


Figure 41: Specific additional CO2 emission for different study cases

9 Conclusions

9.1 Calcium looping thermal integration with coal power plant

The calcium looping process had been designed and simulated to be able to capture 90% of the CO_2 in the flue gases from a reference coal power plant. Three different integration options were proposed for integrating the thermal streams of the process to a steam cycle, one with a separate simple steam cycle for the calcium looping, one with a bit more complex steam cycle but still separate and one option with integration of the calcium looping process in the same steam cycle as for the reference power plant. Additionally a simulation and subsequent integration modelling of an oxy-fuel combustion process was carried out to have a competing technology for comparison.

The case were both the reference plant and the calcium looping plant were integrated into the same steam cycle was shown to be the alternative with the lowest penalty to electrical efficiency of the whole plant, with oxy-fuel technology being the second best alternative from an efficiency point of view.

9.2 Cement plant integration

An interesting system of power plant, calcium looping and cement plant was also investigated here. The benefits resulting from a limestone free cement plant in this system are even stronger then the benefits in a standard cement plant as the presented base case. The benefits are the reuse of spent sorbent of the calcium looping process, reduction of the CO_2 emission and the increasing power production.

As the presented and discussed results have shown, both study cases of the combination of cement plant, power plant and a calcium looping process have significant benefits as both make use of these benefits to a large percentage.

The reduction potential of limestone and CO_2 emissions are high and basically results from the replacement potential of fresh limestone by the purge from the calcium looping process. More benefits are the increasing power production and very low differences in the scaling factor of the calcium looping process for a combination of power production and cement production, which means especially for the limestone free cement plant, that the cement production is nearly for free due to the extreme reduction of raw materials. The additional energy demand rises from the base case to the integrated cement plant but is at its lowest for the limestone free cement plant which again is noticed in the electrical efficiency. The efficiency penalty compared to the coal power plant with calcium looping is low.

Within these beneficiary systems the raw material consumption for limestone can be minimized for power production and cement production if those processes are connected with a calcium looping process as shown in this thesis. The plants can be sized to fulfil the needs of power production, cement production and CO_2 capture to its optimum while saving raw materials such as limestone and coal. The specific coal consumption regarding clinker and electricity can be held at a low level with a when the cement plant is chosen to be sufficient small compared to the power plant and a very low efficiency penalty will be achieved.

Considering the power plant with calcium looping process is an economical feasible choice, the combination with a calcium looping plant will be more cost-effective than two separated plants for power and cement production. The reason for this is to be found in the described beneficiary system and the share of technology, e.g. the calcium looping process is working as a calciner for the cement plant.

Due to all these benefits it is strongly recommended to consider an integration of the cement plant into the system of power plant and calcium looping process to make use of the benefits stated above.

From the presented results the case of the limestone free cement plant is recommended as benefits in all comparisons can be found. Merely the additional specific power generation is lowest in this case whereas the electric efficiency is at its highest.

10 Future work

To fully understand the potential of calcium looping technology as a post-combustion technology for carbon capture it is suggested to make further investigations on this topic.

Future work into this area of calcium looping technology is suggested to make more investigations into the economic aspects of choosing calcium looping before other competing alternatives and between different configurations of integration of to the steam cycle. Other work in for calcium looping as a post-combustion process should focus on finding solutions to minimize the efficiency penalty specific to the usage of auxiliary energy need as this contributes to a severe reduction in the electrical efficiency of the plant after integration of calcium looping.

Investigating calcium looping as a pre-combustion capture technology compared to other competing technologies is one area that should receive more attention and may be a possible outlet for further investigation.

For future investigation concerning cement plant integration it is suggested to research on an optimum of the sizing of power plant and cement plant to achieve the best possible combination of all effects such as electrical efficiency, coal consumption, CO_2 capture efficiency and limestone replacement. In favour of that, a cement plant should be chosen with all data available for all streams.

An interesting aspect could also be the reduction potential of CO_2 emission by using only the purge from a calcium looping process without recirculating the flue gases to the calcium looping process. This case can represent two plants in different locations where the purge is transported to the cement plant.

Another important research area will be to build up a study case with fuel replacement in the cement plant to biofuels. A replacement of fuel will lead to a more sustainable process and even to a negative release of CO_2 as biomass is considered to be close to CO_2 neutral and the calcium looping process captures most of the CO_2 emissions released in the production.

The encouraging results received in this thesis work make it also very interesting to investigate about the potentials of an integration of calcium looping in other limestone consuming processes such as the pulp and paper processes.

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