Institute of Combustion and Power Plant Technology







Director: Prof. Dr. techn. G. Scheffknecht Pfaffenwaldring 23 • 70569 Stuttgart Phone +49 (0) 711-685 63487 • Fax +49 (0) 711-685 63491

Diploma Thesis No. 3239 cand. mach Emmanouil Stavroulakis

Experimental investigation of the effect of water vapour on the Ca-looping process at a 10kWth Dual Fluidized Bed facility

Address: Pfaffenwaldring 46b, 70569 Stuttgart

Date of issue:01.03.2013Date of submission:01.09.2013Supervisor:Dipl.-Ing. Glykeria Duelli (Varela)

Institut für Feuerungs- und Kraftwerkstechnik



Universität Stuttgart



Direktor: Prof. Dr. techn. G. Scheffknecht Pfaffenwaldring 23 • 70569 Stuttgart Tel. +49 (0) 711-685 63487 • Fax +49 (0) 711-685 63491

> Stuttgart, 01.03.2013 Prof. Sch./Du.

Diploma Thesis Nr. 3239 for Mr. Emmanouil Stavroulakis (ERASMUS-Programm) Matr.-Nr. 2840488

Experimental investigation of the effect of water vapour on the Ca-looping process at a 10kWth Dual Fluidized Bed facility

Motivation:

Climate change phenomena are attributed to the increasing CO_2 emissions. Since power generation is expected to rely on fossil fuels in the near future, a feasible technique to mitigate the CO_2 emissions is necessary. Calcium looping is a promising post-combustion CO_2 capture process, utilizing limestone as sorbent. In this frame IFK has built a 10 kW_{th} dual fluidized bed facility, where parametric investigations take place.

Process Description:

Wet flue gases are directed in a fluidized bed carbonator operating at temperatures around 650° C where CO₂ is absorbed from lime and a CO₂ lean flue gas is released to the atmosphere. The solids leaving the carbonator are directed to a second fluidized bed reactor where regeneration of lime takes place at temperatures around 900°C. The carbonation/calcination reaction is the following:

 $CaO + CO_2 \leftrightarrow CaCO_3$, $\Delta H = \pm 178 \text{ kJ/mol}$

The necessary heat for the endothermic calcination reaction is provided by oxy-fired combustion of coal which implies high concentrations of water vapor and CO_2 . The captured CO_2 is recovered in concentrated form and is suitable for purification and compression.

Study's scope:

In the framework of this diploma thesis experiments were performed to study the effect of water vapour on the process. The approach involved literature review and evaluation of the experimental data regarding the following aspects:

- 1. Lime performance in terms of
 - a. chemical properties: changes of the average CO₂ capture capacity and the microstructure i.e. surface area and porosity.
 - b. mechanical properties: changes of the sorbent particle size and the attrition phenomena.
- 2. The efficiency of the carbonator and the regenerator in terms of CO₂ capture and release efficiency.
- 3. Material losses and estimation of the essential make-up flow.

The diploma thesis is supervised by *Miss Dipl. Ing. Glykeria Duelli*. The work is performed according to the IFK Guidelines for Diploma thesis.

 Beginn der Arbeit:
 01.03.2013

 Abgabetermin:
 01.09.2013

(Prof. Dr. techn. G. Scheffknecht)

Amm

(Dipl.-Ing. Glykeria Duelli)

Adresse/Kontaktdaten Student: Adresse: Pfaffenwaldring 46b, 70569 Stuttgart Email: stavroulakisem@gmail.com Tel: 01799536697

Abstract

Carbon Dioxide (CO₂) is the main factor held co-responsible for the global warming and the climate change through the greenhouse effect mechanism. CO₂ is mainly produced by coal fired power plants around the globe and shows a constantly increasing tendency. Post-combustion CO₂ capture based on the Ca-looping process is a promising technology under development, based on the carbonation reaction between CaO and CO2 to form CaCO₃ and the regeneration of CaO by calcination of CaCO₃, producing a rich CO₂ stream. This work is focused on the study of the effect of water vapour - steam on the Ca-looping process, since H₂O is contained in coal and therefore in the flue gases of the power plant. Moreover H₂O is expected to be found in the regenerator due to the oxy-fired combustion of coal in order to acquire the essential calcination energy. A dual fluidized bed facility was used for the purposes of this study. A CFB reactor operating at 630°C was utilized as the carbonator and a BFB reactor operating at 900 to 920°C as the regenerator. Results showed increased reactivity of the sorbent in terms of CO₂ capture capacity, namely maximum carbonation conversion – X_{max} for all cases when steam was present. Moreover noticeable increase of the carbonator CO₂ capture efficiency was achieved with significantly lower looping ratios and space times in comparison with previous experiments were no water vapour was present. Regarding the regenerator performance it was found that high sorbent calcination degrees, more than 80% were achieved. In terms of attrition significantly higher material losses were recorded in comparison to previous experiments without water vapour presence.

Table of Contents

AbstractIV			
Table of ContentsV			
List of Figures			
List of TablesIX			
NotationX			
AbbreviationsXII			
1 Introduction 1			
2 Background			
2.1 Carbon Dioxide – CO ₂ Emissions			
2.2 Carbon Capture and Storage Technologies – CCS 6			
3 The Calcium Looping Process			
3.1.1 State of the Art			
3.1.1.1 Ca-looping Process Realisation			
3.1.1.2 Desulfurization and Coupling with the Cement Industry			
3.1.1.3 Fluidized Bed Technology12			
3.1.1.4 Current Status of Process Development			
3.1.2 The Carbonation-Calcination Reaction			
3.1.3 Sorbent Chemical and Mechanical Properties17			
3.1.3.1 Sorbent Activity17			
3.1.3.2 Mechanical Properties21			
3.2 Thesis Statement			
4 Methodology and Experimental Procedure			
4.1 Experimental Matrix25			
4.2 Description of Facility and Experimental Procedure27			
4.3 Laboratory Analysis29			
4.4 Measured and Calculated Parameters31			
5 Results, Discussion and Conclusion			
5.1 Quality of the Experimental Data			

	5.1.	.1 Steady States and Mass Balance	33
	5.2	Maximum Carbonation Conversion of the Sorbent (X _{max,ave})	36
	5.3	Surface Area of the Sorbent	41
	5.4	Carbonator Performance	43
	5.5	Regenerator Performance	47
	5.6	Comminution Phenomena	51
6	Sur	nmary	64
7	Bibliography66		
8	Annex71		

List of Figures

Figure 2.1: World energy-related CO ₂ emissions, source [8]	4
Figure 2.2: CO ₂ emission mitigation goals, source [11]	5
Figure 2.3: Basic CCS Technologies, as modified from [5]	7
Figure 2.4: Sequestered versus avoided CO ₂ schematic, [14]	7
Figure 3.1: Schematic of a Ca-looping system for CO2 capture from a power pla	ant, [7]10
Figure 3.2: Capture cycle general layout [18]	10
Figure 3.3: a) Bubbling Fluidized Bed [25] b) Circulating Fluidized Bed, as modi	fied from [26]
	12
Figure 3.4: Thermodynamic Equilibrium Curve [30]	14
Figure 3.5: H ₂ O thermodynamic equilibrium	15
Figure 3.6: Sorbent Deactivation Curve	18
Figure 3.7: Schematic of sintering progression during cyclic calcination and carb	oonation19
Figure 3.8: Relationship between sorbent morphology and conversion [33]	21
Figure 3.9: The two different attrition mechanisms: abrasion and fragmentation,	[53]22
Figure 4.1: Facility Drawing	27
Figure 4.2: Carbonation Curve	30
Figure 5.1: Experimental Points - Steady States on the Thermodynamic Equilibre	ium Curve33
Figure 5.2: Carbonator Mass Balance	34
Figure 5.3: Regenerator Mass Balance	35
Figure 5.4: Example of Steady State for the Carbonator	35
Figure 5.5: Example of Steady State for the Regenerator	35
Figure 5.6: a) Maximum Carbonation Conversion versus cumulative H ₂ O/Ca	b) Maximum
Carbonation Conversion versus H ₂ O partial pressure	37
Figure 5.7: Maximum Carbonation Conversion versus cumulative H ₂ O/Ca	38
Figure 5.8: The effect of water vapour partial pressure on X _{max,ave}	38
Figure 5.9: Maximum Carbonation Conversion versus Theoretical Cycles	40
Figure 5.10: Maximum Carbonation Conversion versus experimental time	40
Figure 5.11: Surface Area	41
Figure 5.12: Surface Area Decrease Rate S _{final} /S _{original}	42
Figure 5.13: a) Surface Area versus cumulative H ₂ O/Ca b) Surface Area versu	us cumulative
CO ₂ /Ca	43
Figure 5.14: Xcarb versus residence time of the carbonator	44

Figure 5.15: Carbonator Schematic	44
Figure 5.16: Carbonator efficiency versus looping ratio and space time	45
Figure 5.17: Experimental carbonator efficiency versus model carbonator efficiency	46
Figure 5.18: Carbonator efficiency versus active space time	47
Figure 5.19: Conversion of CaCO ₃ to CaO versus water vapour partial pressure	48
Figure 5.20: Conversion of CaCO ₃ to CaO versus cumulative moles of H ₂ O/mol Ca	49
Figure 5.21: Regenerator efficiency versus regenerator load	50
Figure 5.22: Mass loss per hour for different experimental conditions	52
Figure 5.23: Material loss per CO ₂ moles for different experimental conditions	53
Figure 5.24: Attrition expressed in make-up flow per circulation rate F0/FCa	54
Figure 5.25: a) 'Cement' formation side one b) 'Cement' formation side two	55
Figure 5.26: Particle size for raw limestone, carbonator bed and circulating sorbent	56
Figure 5.27: Particle size for EnBW limestone and two raw calcined material samples	57
Figure 5.28: Particle size for raw calcined material, carbonator and regenerator bed	57
Figure 5.29: Particle size of the regenerator bed for three different experimental cases	58
Figure 5.30: a)Raw limestone EnBW b)Calcined raw material	59
Figure 5.31: Regenerator bed	59
Figure 5.32: Median value of particle size – dp_{50}	60
Figure 5.33: Regenerator bed after an experimental set	61
Figure 5.34: Median value of particle size – ULS samples versus experimental time (C	O ₂ in
the Carb)	62
Figure 5.35: Median value of particle size – LLS samples	63
Figure 8.1: a) 36ULS sample one, 2 nd set with steam in Reg-900°C	71
Figure 8.2: a) Crack that could lead to attrition by fragmentation b) Example of impur	ity of
the sorbent	71
Figure 8.3: a) Candle filters - exit of carbonator b) 2 nd cyclone - exit of carbonator	71
Figure 8.4: a) Sample 18LLS-1 st set, steam in both carbonator and regenerator-900°C	
b) Sample 53LLS-3 rd set, steam in the regenerator-920°C	72
Figure 8.5: a), b) Agglomeration in the 1 st cyclone of the regenerator	72
Figure 8.6: Carbonator bed, 1 st experimental set, steam in Carb and Reg	72
Figure 8.7: a) 2 nd cyclone of the carbonator b) Calcined raw material	73
Figure 8.8: Matlab result for TGA calcination measurement	73
Figure 8.9: Matlab result for TGA carbonation measurement	74

List of Tables

Table 2.1: Greenhouse Effect Gases [5]	3
Table 2.2: CO2 emission factors, as modified from [5]	4
Table 2.3: Sequestrated versus avoided CO2 [5]	8
Table 4.1: Experimental Plan	25
Table 4.2: Flue gas composition for typical hardcoal as per (d.adry air, h.ahumid air)	26
Table 4.3: Limestone utilized	27
Table 5.2: Bulk density of the sorbent	61

Notation

A	Area	m²
D	Diameter	m
dp ₅₀	Median particle size	μm
FCa	Molar flow of Ca circulating between the reactors	kg/h or mol/h
FCO ₂ inlet	Molar flow of CO2 entering the carbonator	Nm³/h or mol/h
FCO ₂ outlet	Molar flow of CO2 leaving the carbonator	Nm³/h or mol/h
F _o	Make-up flow	kg/h or mol/h
E_{carb},E_{CO^2}	CO2 capture efficiency	-
E _{CO2equil}	Equilibrium CO ₂ capture efficiency	-
E _{reg}	Efficiency of the regenerator	-
g	Acceleration of gravity	m/s²
X _{carb}	Sorbent carbonate content entering the regenerator	mol CaCO3/mol Ca
X _{calc}	Sorbent carbonate content exiting the regenerator	mol CaCO3/mol Ca
X _{max, Xave}	Maximum carbonation conversion	mol CaCO3/mol Ca
X _N	CO2 carrying capacity at carbonation/calcination cycle N	mol CaCO3/mol Ca
Ceq	Equilibrium CO ₂ concentration	-
	CO ₂ concentration	-
$\overline{C_{CO_2}}$	Logarithmical average CO2 concentration	-
V	Volume	m³
LR	Looping Ratio	-
m, W	Mass	kg
NCa	Molar mass of Ca	mol
n	Moles	mol
Р	Pressure	mbar
t _{res(Carb)}	Residence time of solids in the carbonator	min
t _{res(Reg)}	Residence time of solids in the regenerator	min
fa	Fraction of active particles reacting in the fast	
	reaction regime	-
S	Specific Surface Area	m²/g
So	Original Specific Surface Area	m²/g
S _f	Final Specific Surface Area	m²/g
t*	Necessary time for achievement of Xmax value	S
Tactive	Active space time	h

T _{space}	Space time of solids in the carbonator	min
dx/dt	Carbonation reaction rate	s ⁻¹
FCa/FCO2	Calcium looping ratio	-
ks	Surface carbonation rate constant	s ⁻¹
ksФ	Apparent carbonation rate constant within the carbonator	
	reactor	s ⁻¹
Nth	Theoretical number of cycles	-
Т	Temperature	°C
Tcarb	Average carbonator temperature	°C
Treg	Average regenerator temperature	°C
yCO2in	CO2 inlet concentration	-
yCO2out	CO2 outlet concentration	-
Fgas	Total flow of gases	Nm³/h
U	Velocity	m/s
ΔΡ	Pressure drop	mbar
Φ	Contact factor	-
ρ	Density	kg/m³

Abbreviations

- ASU Air Separation Unit
- BAT Best Available Technology
- BET Brunauer Emmett Teller
- BFB Bubbling Fluidized Bed
- Carb Carbonator
- CCS Carbon Capture and Sequestration
- CFB Circulating Fluidized Bed
- CV Cone Valve
- DFB Dual Fluidized Bed
- EU European Union
- GHG Greenhouse Gases
- IGCC Integrated Gasification Combined Circle
- LLS Lower Loop Seal
- LPM Litres per minute
- MFC Mass Flow Controller
- PSD Particle Size Distribution
- Reg Regenerator
- TGA Thermo-Gravimetric Analyser
- ULS Upper Loop Seal

1 Introduction

Human-induced Carbon Dioxide (CO₂) concentrations in the atmosphere are globally accepted as the major cause of the climate change through enhancement of the greenhouse effect, leading to global warming. Monitoring has shown that the concentration of CO₂ in the atmosphere, reached a level of 389 ppm by 2010, and further increased to 391 ppm in 2011. This is an increase of approximately 112 ppm (around +40 %) compared to pre-industrial levels [1]. Energy-related CO₂ emissions account for nearly 60 percent of total global anthropogenic GHG emissions. In 2011, CO₂ emissions from the combustion of fossil fuels reached a record of 31.6 Gt [2]. Primary energy consumption continues to rise and fossil fuels have provided the major share of the incremental growth over the past decade, accounting for more than 80 percent of the increase in energy consumption [3]. As a result the development of CO₂ mitigation technologies has been deemed essential and steps towards this direction have been made during the last few years. Overall it is estimated that the European Union will be emitting some 4.2 billion tonnes of CO₂ annually by 2030. According to the European commission 10% of these emissions could be avoided using CCS technologies. Specifically it is estimated that around 400 million tonnes of CO₂ per year could be avoided through CCS by 2030 and around 1.7 billion by 2050 depending on the extent of use of CCS technologies. Moreover up to 12 CCS-equipped power plants are to be operational in the EU by 2015 [4].

Calcium looping is one of the most promising Post-combustion CO₂ capture technologies, which presents some advantages that render it more attractive in comparison to other potential solutions. Such are the relatively easy integration in existing power plants and a low efficiency loss. This technique can yield a highly pure stream of CO₂ of 85 to 95% [5]. It is based on the Ca-looping process. During this process a carbonation reaction takes place between CaO – Calcium Oxide and CO₂ to form CaCO₃ - Calcium Carbonate. As a result a CO₂ lean stream leaves the carbonator reactor. Thereafter the regeneration of CaO is achieved by the calcination of CaCO₃ and a rich CO₂ stream that leaves the regenerator reactor is produced. That rich stream is then compressed and stored. The regeneration reaction is responsible for the energy penalty of this process, since it is an endothermic reaction that requires energy input to maintain the high temperatures essential.

This work is focused on the study of the effect of water vapour – steam on the Calooping process. The effect of steam is an essential part of this process yet to be studied. The reason is that H₂O is contained in coal and therefore in the flue gases of the power plant As a result an atmosphere of steam partial pressure is expected in the carbonator. Moreover H₂O is expected to be found in the regenerator, due to the oxy-fired combustion of coal in

order to acquire the essential calcination energy. The presence of steam inside the reactors could reach high levels depending on the type of coal utilized, e.g. lignite is expected to yield high steam partial pressure due to its increased moisture content. The possible enhancing or retarding effect of water vapour on the carbonation and calcination is to be studied during this thesis, as well as a possible combined effect of steam present in both reactors. The approach involved literature review, experimental investigation and data analysis and evaluation regarding the aspects of: (i) lime performance in terms of chemical and mechanical properties, (ii) the efficiency of the carbonator and regenerator in terms of CO_2 capture and release efficiency and (iii) material losses and estimation of the essential make-up flow of sorbent. In conclusion this work falls within the limits of a diploma thesis. Further and more thorough work is yet to be done in order to be able to fully understand the complex effect of steam.

A dual fluidized bed facility is used during the experiments of this thesis [6]. In particular a Circulating Fluidized Bed is utilized as the carbonator reactor and a Bubbling Fluidized Bed as the regenerator reactor. The CFB is utilized as the carbonator reactor due to the better contact factor it presents in comparison to the BFB. The carbonator operates at a temperature of 630°C in all cases, whereas the regenerator at temperatures of 900°C and 920°C.

2 Background

2.1 Carbon Dioxide – CO₂ Emissions

Carbon Dioxide (CO_2) is a natural part of the air in the atmosphere with a volumetric concentration of around 3%. Although it is not a pollutant it is held co-responsible for the global warming and the climate change through the greenhouse effect mechanism.

Normally CO_2 is produced by the decomposition of biomass in great portions in nature, but is balanced by the amount of CO_2 also needed for the former building of this biomass. The fossil fuels widely used for energy production, also occurred through the decomposition of biomass millions of years ago. However the burning of these fossil fuels in power plants releases great portions of the CO_2 that was held within, thus creating the imbalance of CO_2 concentration in the atmosphere. Those CO_2 emissions for industrial reasons are also known as anthropogenic or energy related.

The reduction of CO_2 emissions is possible by energy saving, increase in the efficiency of power plants through utilization of new technologies, switch to fuels with lower carbon content as well as by the utilization of renewable energy technologies. Alternatively there is the upcoming technical solution of CO_2 sequestration and storage, known as CCS, Carbon Capture and Storage technology.

The following table presents the greenhouse effect gases and their share on the phenomenon. It is observed that CO_2 contributes more than half to the effect and thus the need to primarily mitigate the CO_2 emissions.

Greenhouse Effect Gases			
Greenhouse Gas	Origin	CO ₂ Equivalent	Share on Greenhouse Effect (%)
Carbon Dioxide CO ₂	Combustion processes	1	64
Methane CH₄	Dumping Grounds, Gas Industry	21	20
Nitrous Oxide N ₂ O	Dumping Grounds, Fertilizer Factories	310	6
Fluorocarbons	Aluminum Production	11300	
Halogenated Hydrocarbons HFC	Refrigerants, Chemical Industry	6500	10
Sulfur Hexafluoride SF ₆	Industrial Processes	23900	

 Table 2.1: Greenhouse Effect Gases [5]

Regarding the fossil fuels used for energy production that release CO_2 , coal is the main one [7]. This is because it is the most abundant fossil fuel, with evenly distributed resources all over the world in comparison to oil or natural gas. It is also cheaper and easier to mine in most cases. Consequently coal is expected to be a prominent fuel for energy production for the next decades.

The largest power plants in MW of energy production worldwide use coal as their main fuel, whereas fossil fuels in general account for more than 80% of the primary energy consumption globally [7]. The following figure presents the world energy related CO_2 emissions by fuel billion metric tons up to present times and future projections until 2040.



Figure 2.1: World energy-related CO₂ emissions, source [8]

The following table presents the CO_2 emission factors for various fuels. It is observed that coal yields the highest CO_2 emissions, especially the brown coal or lignite, in comparison to oil or natural gas. However, to the extent that coal cannot be replaced due to feasibility or economy related reasons by fuels that yield lower CO_2 emissions, CCS technologies provide a viable solution.

Table 2.2: CO₂ emission factors, as modified from [5]

CO ₂ emission factors for various fuels			
Fuel	CO ₂ emission factor		
ruei	kg/GJ	t/GWh	
Hard coal	94.5	340.2	
Raw brown coal	110	397.2	
Brown coal dust	99	356.4	
Heating oil	76	273.6	
Natural gas	56	201.6	

2 Background

In particular CCS technologies have a great potential to contribute for stabilization of the concentration of greenhouse gases in the atmosphere in the mid to long term [9]. Moreover their application is focused on large sources of CO_2 like power plants or cement plants and refineries. Finally considering the recent increases in coal consumption among the power generation sector and the immediate projections for coal use as primary energy resource in the upcoming years, the need of application of such technologies will be reinforced [9]. In addition the CO_2 mitigation and the implementation of such technologies is promoted by the EU proposal for a CO_2 emissions trading system in Europe [10], whereas goals such as the 400ppm scenario are set as presented in the figure below. The dashed and continuous lines represent different approaches.



Figure 2.2: CO₂ emission mitigation goals, source [11]

2.2 Carbon Capture and Storage Technologies – CCS

CCS refer to the long-term isolation of fossil fuel CO_2 emissions from the atmosphere through capturing and storing the CO_2 deep in the subsurface of the earth.

They consist of three key stages:

- Capture: Carbon capture is the separation of CO₂ from the other gases produced when fossil fuels are burnt for power generation or from gases produced in other industrial processes.
- 2. Transport: Once separated, the CO₂ is compressed and transported to a suitable site for geologic storage.
- 3. Storage: CO₂ is injected into appropriate storage sites, deep underground rock formations, often at depths of 1 km or more.

Carbon Capture

The main step of the CCS technologies is CO_2 capture. Depending on whether CO_2 is captured downstream, upstream or during fuel combustion three groups of technologies are distinguished [5]. These are post-combustion, pre-combustion and oxy-fuel combustion respectively. The post-combustion option demands little modifications to the current power generation facilities. The main processes considered for this option are calcium looping that takes place at high temperatures and relies on the use of limestone, a cheap and abundant sorbent and solvent scrubbing [12] that takes place at lower ambient temperatures. Several solvents aqueous and others have been proposed for the latter option. The pre-combustion option involves fuel gasification under pressure with CO_2 separation. The H₂ rich gas is used thereafter for power generation through a combined cycle process scheme or through fuel cells [13]. The Integrated Gasification Combined Cycle is the most advanced process under this category. This technique has a respective efficiency loss of around 6% and is of greater interest for brown coal fired facilities [5]. Finally the oxy-fuel combustion option involves the combustion of fuel with almost pure O_2 . The O_2 is supplied by an Air Separation Unit ASU. This technique can yield a 98% rich CO₂ stream; however the ASU demands a great portion of power that can lower the overall efficiency by 7 to 10% [5]. The products of oxycombustion are primarily carbon dioxide and water, which can be easily condensed to generate a highly pure CO₂ stream. In general, the advance of a technological option over the others takes into account the current technological maturity, the respective energy efficiency penalty and the costs per ton of CO_2 avoided and of electricity generation.

The three basic CO₂ capture technologies developed are schematically presented below:



Figure 2.3: Basic CCS Technologies, as modified from [5]

A reasonable question that could be raised is whether the additional CO₂ that occurs, through the production of power that the CCS technology requires, actually exceeds the CO₂ sequestrated by this technology. The power required for the CCS facility is expected to derive from additional coal burning and therefore additional CO₂ release. The concept in question is schematically presented in the figure below.





However as shown in the following table the quantity of sequestrated CO_2 always exceeds the avoided CO_2 .

		Hard Coal Facility according to	
Feature	Unit	BAT	
		without CCS	with CCS
Fuel emission factor	tCO2/MWhвг	342	
Net efficiency	%	45.6	33.6
CO2 in raw flue gas	tCO2/Mwel	750	1018
Grade of sequestration	%	0	90
Sequestrated CO ₂	tCO2/Mwel	0	916
Emitted CO ₂	tCO2/Mwel	750	102
Avoided CO ₂ 750 tCO ₂ /MWeI	tCO2/Mwel	0	648
in % respectively on 750 tCO2/MWel	%	0	86

Table 2.3: Sequestrated versus avoided CO₂ [5]

CO₂ Transport and Storage

The total cost of CCS technologies is additionally encumbered by the cost of CO_2 transport and storage. The transport of CO_2 can be quite costly since it has to be pressurized due to the respective large volumes produced. The critical point for CO_2 compression lies at 73.9 bar/ 31.1 °C, however due to impurities and possible pressure loss during transport the CO_2 is compressed at 110 to 114 bar [5]. The transport could be ideally handled by a pipe-line network similar to that used for natural gas, or if this is not achievable in short terms like in the case of Europe where there is not a CO_2 pipe network built, it could be handled by common means of transport e.g. train or ships similar to LNG-carriers for near coast regions.

Furthermore for the storage of CO₂ stable geological formations are proposed, possibly old mines of a depth of over 800m so that the CO₂ remains in hypercritical liquid condition due to the high pressure. Such formations are believed to be a safe option not involving a danger of leakage, since they have held natural gas reserves for millions of years. The total retaining capacity of such formations has not been conclusively clarified; however it is estimated that the European storage capacity is around 120 billion tonnes and not smaller than 40 billion tonnes. Taking into account that EU will need to store around 20 billion tonnes between now and 2070, the minimum storage capacity should cover in double the storage needs until then [4]. Another way to store and concurrently leverage the sequestrated CO₂ is to utilize it in oil or natural gas mining. A pump would lead the pressurized CO₂ underground into the supposed oil deposit. Thus the CO₂ would displace the oil, providing the essential pressure to lead it to the surface. A similar mechanism could be applied for natural gas. After the deposit is drained it could be sealed to hold there the non-desired CO₂.

3 The Calcium Looping Process

As mentioned above among the different CCS technologies the post combustion Ca-Looping Process is rapidly developing the last years [9]. This technology presents some clear advantages that make it favourable against other CO_2 capture processes. Such are:

- Lower energy penalty of around 2.75%, without the inclusion of CO₂ compression, in comparison to other technologies that present efficiency losses around 10-14%. [15]
- The sorbent utilized is limestone that is of relatively low price and can be found in large quantities worldwide.
- The Ca-Looping process is based on the existing technology of Fluidized Beds which is tested and used in the industry.
- It can easily be integrated to the current power plants in comparison to other processes, since it is a post-combustion technology.
- It has been proposed to work also as a desulfurization unit since SO2 can be captured by CaO.
- The deactivated sorbent can be used in the cement industry, lowering the cost of cement production. [16]

3.1.1 State of the Art

3.1.1.1 Ca-looping Process Realisation

The following schematic presents the Calcium Looping process in simple terms, as it would be incorporated in a power plant to capture typical CO_2 concentrations between 10 and 15% [17]. The flue gas from the power plant enters the carbonator where the CO_2 capture takes place. A CO_2 lean gas stream exits the carbonator, whereas the solids proceed to the regenerator. There the CO_2 is released and a CO_2 rich stream exits the regenerator, ready for compression and storage. The high temperatures in the regenerator are achieved by the oxy-fired combustion of coal. The flue gas, the CO_2 rich and lean stream can be noticed, as well as the solid flow between the fluidized beds, the make-up flow and the ASU.



Figure 3.1: Schematic of a Ca-looping system for CO₂ capture from a power plant, [7]

As presented in the following figure the Ca-looping system implemented to the power plant, can incorporate a supercritical steam cycle to take advantage of the significant amount of heat occurring in several parts of the system.



Figure 3.2: Capture cycle general layout [18]

The carbonation is an exothermic reaction that offers energy to be integrated in the steam cycle in two possible ways. The first one is symbolized as Q_1 in the figure and would involve water walls that would absorb the heat surplus occurring in the carbonator and at the same time control the temperature reaction. The second one would absorb the heat from the solids coming out of the regenerator, reducing their temperature before they enter the carbonator. Moreover the utilization of heat from the CO₂ poor stream leaving the carbonator at 650°C as well as from the rich CO₂ stream leaving the regenerator at 900°C could offer additional energy symbolized as Q_2 and Q_3 respectively in the figure. Finally the extraction of sol-

ids from the regenerator consisting of deactivated sorbent, coal ashes and CaSO₄, could also contribute to the steam cycle since they have a high exiting temperature. The heat they offer is symbolized as Q_4 in the figure.

The above incorporations could compensate partially for the cost of the Ca-looping process, for example provide with the energy for the air separation unit – ASU, the CO₂ compression unit and the various pumps and equipment of the system. Finally the capture system could generate additional power with an efficiency of 26.7% in relevance to the coal input of the regenerator for oxy-fuel combustion, without disturbing the efficiency of the main power plant steam cycle. The capture cost would be approximately 16 \in /ton of CO₂ avoided [18].

3.1.1.2 Desulfurization and Coupling with the Cement Industry

One of the benefits of the Ca-Looping technology for CO_2 capture is the possible coupling with flue gas desulfurization. Instead of utilizing a separate unit, the CaO could capture the SO₂ in the flue gas through the reaction:

$$CaO + SO_2 + \frac{1}{2}O_2 \rightarrow CaSO_4$$

to produce $CaSO_4$, also known as gypsum. However the SO_2 absorption is an irreversible reaction at the respective temperatures in the regenerator; SO_2 gradually reduces the CO_2 capture capability despite the very low SO_2 concentrations in ppm, so there would be an increase in the essential make-up flow. On the other hand the carbonation/calcination cycles increase the pores of the material with a size suitable for SO_2 capture, enhancing the SO_2 capture.

An additional benefit of the Ca-looping process technology is the possible coupling with the cement industry. The deactivated CaO and coal ashes, along with CaSO₄ formed by the potential desulfurization process, that are extracted from the regenerator could be fed into the clinker oven [16]. The cement industry generates approximately 5% of the global CO_2 emissions, whereas the cement production seems to be constantly growing [19], [20]. As a result a lot of research has been carried out concerning the reduction of CO_2 emissions from existing and new cement plants [16], [21]. Calcined limestone, CaO, is the main precursor to cement and is fed to the kiln for clinker production. Moreover limestone calcination is responsible for 70% of the power required. The energy required for calcination and the related CO_2 emissions can be avoided by feeding calcined limestone into the kiln, originating from the purge flow removed from the calciner of a Ca-looping facility due to sorbent decay and the respective make-up flow required. An integration of CO_2 -free power production and clinker production has been shown to be feasible, leading to large economic savings [21].

3.1.1.3 Fluidized Bed Technology

The fluidized bed technology utilized for the Ca-looping process is a well-known technology used in various applications in chemical industry and combustion processes [22], [23], [24]. Fluidized beds are reactors based on gas-solid contact to transfer heat and mass. They present particular advantages such as better contact factor and homogeneity in heat transfer.

There are different types of fluidized beds depending on the fluidization velocities utilized. The bubbling fluidized bed is a reactor that utilizes low fluidization velocity. The material stays within the reactor and forms a high density area in the bottom and a freeboard area above, that the fluidized solids do not overcome. Large gas bubbles are formed within the solid bed that bypass the solid-gas reaction and cause a moderate contact factor and therefore worse reaction conditions, as far as the carbonation reaction is concerned. Regarding the calcination reaction the decisive factor is the heat transfer and homogeneity, so that the appropriate conditions for the sorbent to release the CO_2 are achieved.



Figure 3.3: a)Bubbling Fluidized Bed [25] b)Circulating Fluidized Bed, as modified from [26]

The circulating fluidized bed reactor utilizes high fluidization velocities that result to a better contact factor, thus better reaction conditions, but may cause increased attrition due to abrasion of the sorbent and thus a greater make-up flow. The sorbent is fluidized up to the top of the CFB where it exits the reactor. The solids are separated from the fluidization gas in a cyclone and return through a standpipe to the bottom of the reactor to be fluidized again. Three areas are formed in a CFB reactor [27]: a dense region at the bottom, a lean-core annulus region in the middle and an exit region at the top. Although the density and distribution

of the sorbent varies in these areas, still presents greater homogeneity in comparison to a BFB reactor.

3.1.1.4 Current Status of Process Development

Theoretical studies on the integration of the Ca-looping system in new and existing power plants have shown that the technology could achieve a substantial reduction of around 30% in capture cost and energy penalties in comparison to stand-alone oxy-fired systems [7]. Taking into consideration that solid materials and operating conditions in the FB units are similar to those present in existing large scale CFB combustors, a rapid scaling up of this technology could be expected.

Both lab-scale facilities of $10kW_{th}$ and larger ones pilot-scale facilities in the range of $200kW_{th}$ to $1.7MW_{th}$ are important for the process scale-up. Lab-scale facilities present advantages as far as sorbent characterization and realisation of parametric studies are concerned, whereas pilot-scale facilities are more suited for long duration experiments, close to industrial conditions. With regard to work performed so far in such facilities the following are reported. Cold model studies characterizing reactor fluid-dynamics have been conducted [28]. Moreover lab-scale facilities have conducted parametric studies and have reached CO_2 capture efficiency values of above 90% [6]. The data collected have been used for further analysis, leading to carbonator model validation [27], [29]. Finally state of the art is the pilot plant of 1 MW_{th} that has commenced operation in integration with 'La Pereda' power plant of 50MW_e in Spain, to capture 70-95% of the CO₂ contained in the flue gas from a 1/150 side stream emitted by the power plant [7]. The thermal power input to the regenerator in large scale plants is generally calculated between 0.4-0.55 of the total power input required by the Ca-looping process [7].

3.1.2 The Carbonation-Calcination Reaction

Calcium Looping is the process that utilizes lime in order to capture the CO₂ from flue gases. It is based on the reversible carbonation calcination reaction as:

$$CaO + CO_2 \leftrightarrow CaCO_3$$
 $\Delta H = \pm 178 \text{ kJ/mol}$

The reaction is governed by temperature and partial pressure of CO₂ dependent according to the following diagram:





The above figure presents the thermodynamic equilibrium curve according to which the carbonation–calcination reaction takes place. The curve is given by the equation:

logP(atm) = 7.079 - 8308/T(K) [30]

The Calcium Looping process understandably follows a cyclic pattern of consecutive carbonations and calcinations.





The carbonation reaction takes place in the carbonator at temperatures around 650° C, 15% CO₂ partial pressure and water vapour presence around 8% [18]. The CO₂ reacts with Ca producing CaCO₃ and a CO₂ lean gas flow comes out nearly free of CO₂. It is observed that the higher the CO₂ concentration and the lower the temperature, the more possible it is that the carbonation reaction will take place, of course within the limits set by the previous equation. Regarding the effect of the water presence as can be shown in the

diagram below presenting the H_2O thermodynamic equilibrium curve, no reaction of the Ca with H_2O takes place.



Figure 3.5: H₂O thermodynamic equilibrium

The curve occurs by the equation:

$$P_{H_20}(Pa) = 9 * 10^{11} * \exp(\frac{-12531.5}{T(K)}), \qquad [31]$$

While the following reactions could take place:

$$CaO + H_2O \leftrightarrow Ca(OH)_2$$

 $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

Manovic and Anthony [32] performed carbonation tests in a TGA under 10 or 20% H_2O conditions. Also the samples tested were calcined under a N_2 (800°C) or CO_2 (950°C) atmosphere to explore the influence of different levels of sample sintering and the results obtained were compared with those seen for carbonation in dry gas mixtures. They found that carbonation was enhanced by steam, but this was more pronounced at lower temperatures and for more sintered samples. With increasing temperature and carbonation time, the enhancement becomes negligible because the conversion reaches a maximum value (around 75-80% for samples calcined in N_2) even without steam. Moreover the shape of carbonation profiles and morphology of carbonated samples showed that steam enhances solid state diffusion and consequently conversion during carbonation.

Moreover, **Florin et al** [33] conducted experiments in a small BFB at 900°C for calcination and 650°C for carbonation, with an inlet gas stream containing 15% (v/v) CO2. When steam is present during the carbonation reaction the reaction proceeds more rapidly in the initial stage of the reaction and the maximum reaction rate is higher compared to experiments without steam. The higher maximum reaction rates which may be interpreted as higher capture efficiencies, clearly demonstrate the reduction in the diffusion resistance during carbonation. On the other hand **Linden et al** [34] also conducted experiments using a TGA device studying the steam effect on carbonation. They found that at temperatures of 400°C and 450°C water vapour had an accelerating effect on the conversion of CaO to CaCO3, whereas at 500°C water vapour had a slightly retarding effect.

Additionally, **Lu et al** [35] found that steam during carbonation at a BFB reactor significantly extended the high CO_2 capture efficiency period. On the contrary **Lim et al** [36] showed no appreciable effect of steam on carbonation conversion during tests in a TGA. The same was also demonstrated by **Arias et al** [17] who studied the effect of steam on the fast carbonation reaction rates using a TGA device at 650°C. The conclusion was drawn that steam has no influence on the reaction rate constant.

Finally according to **Yang and Xiao** [31] that conducted experiments in a TGA at 550°C, steam improved the CaO carbonation performance significantly and this was attributed to the catalytic effect of steam on the reaction, rather than to an improvement of the CaO physical properties such as specific surface area and pore structure. The CaO conversions were clearly increased for the same reaction time in the presence of steam.

Thereafter the solids enter the regenerator – calciner where at a higher temperature they release the CO_2 captured [37] according to the reaction:

$$CaCO_3 \rightarrow CaO + CO_2$$
 $\Delta H = +178 \text{ kJ/mol}$

The calcination reaction take place at temperatures around 900°C to form CaO to be directed to the carbonator. From the thermodynamic equilibrium it is observed that the higher the temperature and the lower the CO₂ concentration the more likely it is for the calcination reaction to take place. A CO₂ rich flue gas leaves the regenerator to be compressed and stored. The heat required for the endothermic calcination reaction will be provided by the oxy-fuel combustion of coal which contributes to a richer CO₂ stream coming out of the regenerator. The use of oxygen can raise the combustion temperatures very high to more than 2000°C and therefore a recirculating flow of flue gas is necessary in order to control the temperature and keep it around the desired value of 900°C while it also contributes to the enrichment of CO₂ stream coming out of the regenerator. The concept was first proposed by Shimizu et al [38] and its advantage is that the oxy-combustion CFB technology for CO₂ capture is developed as an independent route and is already a more mature technology in a near-commercial stage. The oxy-fuel combustion involves a high CO₂ partial pressure of around 60% and high water vapour partial pressures up to 30% [9], dependant of the fuel used and the recycle of the gas stream. One of the main drawbacks associated to the oxyfired fuel combustion is the high energy consumption of the air separation unit – ASU, which provides the FB with a stream of almost pure oxygen. Some advanced concepts have been proposed to avoid that cost, such as the utilization of a circulating hot solids stream from an air-fired combustor to the regenerator in order to transfer the essential heating energy [7]. High CO_2 partial pressures can cause sintering thus reducing the sorbent carrying capacity [36] and reduce the calcination rate [39].

Regarding the water vapour effect on the calcination reaction, the following are reported in the literature:

Khraisha and Dugwell [40] performed calcination of limestone in a suspension reactor at different temperatures. They observed that water vapour at a 2.22% level enhanced the conversion achieved in the calcination process, whereas at a 6.09% level produced a retarding effect. The detection of an optimum in the water vapour was attributed either to porosity effects at the surface of limestone particles or alternatively to diffusion effects at increasing air moisture contents. The increased temperature still remained the decisive factor in comparison to water vapour.

Boynton [41] suggested that steam lowers the dissociation temperature of some types of limestone therefore slightly catalysing the rate of calcination. Additionally **MacIntire and Stansel** [42] that performed calcination of limestone fines at 700°C in steam, noticed that deep injection of steam into the limestone was essential to expedite complete calcination. They concluded that the steam effect would be primarily a surface reaction and assumed that an atmosphere of steam might function to catalyse the disruption of the CaO-CO₂ bond.

Wang and Thomson [43] reported that a relatively small steam pressure can significantly enhance the calcite decomposition rate although the enhancement was less significant as steam pressure increased.

Wang et al [44] studied the decomposition of limestone in a FB reactor at a temperature of 920°C for particles of 0.25-0.5 mm size. They reported enhanced decomposition conversion as the steam dilution percentage in the CO_2 supply gas increased, in specific 72% conversion without steam dilution and 98% conversion for 60% steam dilution (40% CO2).

3.1.3 Sorbent Chemical and Mechanical Properties

3.1.3.1 Sorbent Activity

Several carbonation/calcination cycles and the oxy-fired environment of the regenerator lead to the decay of the sorbent. Sorbent activity tends to decrease rapidly at first and less as the carbonation-calcination cycles increase, until it reaches a residual activity [45]. Factors influencing the decay are the following: sintering, attrition, reaction with impurities in the flue or fuel gas. The following equation has been proposed [46] for the calculation of the decay of the sorbent:

$$X_{N} = \frac{1}{\frac{1}{1 - X_{r}} + kN} + X_{r}$$

where Xr, the residual CO₂ capacity and k are empirical constants equal to 0.075 and 0.52 respectively, as estimated by [46]. X_N is the symbol used for maximum carbonation conversion instead of X_{max} when the number of cycles is determined. Plotting the above equation for e.g. N=250 cycles results to the following diagram:



Deactivation Curve

Figure 3.6: Sorbent Deactivation Curve

One of the physical properties affected by the carbonation/calcination reaction is the surface area. In general high surface area means greater reactivity for the sorbent. Studies performed with/without steam presence revealed that as the material gets sintered with time its surface area is expected to be gradually reduced. Surface area loss is characterized by rapid initial rate followed by a slower rate. Also there is an optimum temperature for maximum surface area. Moreover small CaCO₃ particles develop much higher surface areas in shorter times than large particles do. They also achieve their peak surface areas at lower temperatures than larger particles do [47].

Chen et al [48] also reported that the generation of new surface area in the CFB attrition system is proportional to the total excess of kinetic energy (above minimum fluidization) consumed and the attrition time, whereas it decreases exponentially with temperature.

According to **Sun et al** [49] ionic compounds such as CaO mostly sinter because of a volume diffusion or lattice diffusion mechanism. They conducted experiments in a TGA where they noticed that a change in carbonation time had negligible effect on the subsequent calcine structure. This led to the conclusion that lime sintering has no memory of carbonation history for the first cycle or that carbonation makes no contribution to CaO sintering. They reported two different pore sizes in the material small V₁ of less than 220nm and large ones

V2 220-610nm. Also they reported shrinkage of the smaller pores and simultaneous growth in the larger pores. Presumably smaller pores arise due to CO₂ driven off during calcination whereas larger pores due to sintering shifting vacancies from smaller to larger pores, driven by vacancy gradients. On carbonation, solid product CaCO₃ fills pores of small diameters (smaller than 220nm for their work). Once these pores are filled the carbonation reaction becomes product layer controlled and proceeds at a much slower rate, with the carbonation product then slowly filling the larger pores. In simple words the pore volume of the smaller diameter pores determines the achievable extend of carbonation during the fast stage. In conclusion sintering was attributed mainly to calcination. Sintering during carbonation seemed negligible. Moreover a quadratic dependence of sintering on surface area change was suggested. The following figure pictures the above description of pore evolution.



Figure 3.7: Schematic of sintering progression during cyclic calcination and carbonation [49] **a)** 1st calcination with no sintering, **b)** after sintering bimodal PSD, **c)** After carbonation smaller pores filled, **d)** After re-calcination and sintering pores further development

Regarding the effect of water vapour on the sorbent properties, studies performed up to now report the following:

Wang et al [44] studied the decomposition of limestone in a FB reactor at a temperature of 920°C for particles of 0.25-0.5 mm size. The conversion increase observed with N₂ dilution was slower than that obtained with steam dilution, whereas their difference presented a peak at 20% dilution respectively. At 20% steam dilution there was 96% conversion, whereas at 20% N₂ dilution there was 89% conversion. The result was attributed to the different thermal conductivities of N₂ and steam: at 920°C steam presents thermal conductivity of 0.127 W/(mK) whereas, N₂ only 0.071 W(mK). For the carbonation tests at 650°C and CO₂ partial pressure of 0.04 MPa (out of 3.0 MPa), close to 60% carbonation conversion was achieved with the CaO produced by steam dilution, whereas only 40% for the CaO produced in 100% CO₂. Thus it was assumed that the reactivity of CaO was greatly improved by lime-stone decomposition in steam dilution.

Borgwardt [50] reported that both CO₂ and water vapour catalysed the sintering process of the sorbent and that their combined effects were additive. A small concentration of water vapour accelerated the surface area reduction of CaO and markedly reduced the temperature at which surface reduction begins. Additionally a clear effect of both CO₂ and H₂O on the reduction of CaO porosity was reported. Like the surface area effect, the combination of CO₂ and H₂O in the sintering atmosphere had a greater effect than either gas individually.

Anthony et al [51] conducted experiments using a TGA for temperatures from 875°C to 925°C. Steam introduced with calcination was found to increase sorbent reactivity, in particular a 15% concentration was found to have the optimum impact on sorbent carrying capacity. Steam injection for calcination was found to have a smaller effect on sorbent carrying capacity than injection for carbonation. Moreover the sorbent morphology was found to change by steam in calcination resulting in a structure that increases carbonation reactivity, whereas steam in carbonation was found to influence the reaction directly resulting in a larger increase in conversion. The improvement due to steam was confirmed for addition during the initial fast reaction regime or later during the slow diffusion regime. This could be attributed to the hydration of CaO at the surface of the sorbent forming Ca(OH)₂ as a transient intermediate, since Ca(OH)₂ is not thermodynamically stable at temperatures over 600°C, that would lead to a prolonged fast reaction phase of the carbonation and increased initial CO₂ capture. Alternatively it could be attributed to the enhancement of CO₂ mobility due to a reduction in diffusion resistance arising from steam presence.

Arias et al [17] suggested that steam can have a slightly positive influence by increasing the sorbent conversion at the end of the carbonation step, due to a positive influence of steam during the diffusion controlled stage, depending on the limestone tested and its particle size. Out of the two types with sizes smaller than 50µm and between 75 to 125µm respectively, no effect was observed for the former and a slight effect for the latter.

Florin et al [33] conducted experiments in a small BFB at 900°C for calcination and 650°C for carbonation, with an inlet gas stream containing 15% (v/v) CO₂. It was proposed that steam present during calcination promotes sintering and that it produces a sorbent morphology with most of the pore volume associated with larger pores around 50nm, which appear to be more stable than the pore structure that evolves when no steam is present. The presence of steam during carbonation reduces the diffusion resistance during carbonation. Finally the highest reactivity was observed when steam was present for both calcination and
carbonation. Moreover when steam is present during carbonation only, the fine pores are retained, whereas when steam is present during calcination only, the shift towards larger pores is due to steam enhanced sintering. These pores are less susceptible to blockage and thus allow for higher conversion. Conclusively the synergistic effect may be explained through the combination of the large pore and reduction in diffusion resistance effect, allowing for better exploitation of these large pores. The following diagram presents the above schematically:



Figure 3.8: Relationship between sorbent morphology and conversion [33]

3.1.3.2 Mechanical Properties

Attrition of the sorbent is a very important aspect that determines the material loss and therefore the essential make-up flow. There are several factors that influence attrition. In this chapter these factors are reviewed as well as the factor of steam in the regenerator and/or the carbonator.

In fluidized beds the material experiences an abrading or attriting process than slowly decreases the particle size. Initially, particles of irregular shape, containing asperities or sharp edges will attrite at those asperities since the smaller cross sections provide points of stress concentration and will become rounded [52]. Additionally, weaker particles are ex-

pected to break first so the ones left after that will be the stronger ones. Fragmentation also occurs immediately after the injection of particles in the hot reactor, as a consequence of thermal stress due to fast heating of the particles and of internal overpressures due to CO₂ release upon calcination. These aspects lead to a high initial rate of attrition that declines with time [52], [48].

One of the main factors affecting attrition is the fluidization velocity. High velocities will lead to increased abrasion by friction with the reactor walls or between the particles and to stronger impacts of the particles inside the reactors. Besides the FB itself, significant attrition should be expected at the cyclones and the grid jets – fluidization flow distributors since the highest velocities expected in the facility occur there. Chen et al [48] reported linear increase in attrition with time and with the square of the excess gas velocity.



Figure 3.9: The two different attrition mechanisms: abrasion and fragmentation, [53]

Fragmentation called percolative might also occur after calcination and the respective particle voidage increase, since it leads to a loss of connectivity of the solid porous structure [52]. Moreover according to Scala et al [52] that performed calcination experiments in a BFB the dominant comminution mechanism for this case and also for this thesis is attrition by abrasion, rather than any type of fragmentation. They also confirmed the maximum initial generation of fines mentioned earlier, that decays to a steady value, after conversion and particle rounding off are complete. Finally they concluded that attrition is a time dependent rather than a conversion dependent phenomenon, when particle round off is the key factor. The increase in attrition during calcination due to weakening of the structure as CO₂ is lost was also reported in [48].

The initial rapid attrition followed by a stable period of negligible changes in particle size was also confirmed by Gonzalez et al [54], who conducted experiments in a pilot plant of two interconnected CFB reactors. They suggested the attrition rate could be in general affected by properties of the solids such as size, surface, porosity, hardness, cracks, density, shape and particle strength as well as by the characteristics of the reactor, particle velocity and exposure time. Moreover they suggested that particle size reduction is also due to CaO shrinkage, but this phenomenon accounts for less than 5% compared to the effect of attrition.

Another important factor is the temperature of the reactors as reported in [48]. Increased temperature should lead to hardening of the particle, making it attrition resistant. However, high calcination temperature leads to a fall in the capture capacity due to the enhancement of sintering at high temperatures. They also concluded that abrasion was the dominant limestone particle attrition factor for the small CFB reactor they used. The effect of temperature could also be attributed to a decrease of gas/particle velocities at higher temperatures for the same bed superficial velocity and to an increase in the threshold particle attrition velocity.

Regarding the factor of CO₂ partial pressure in the reactors, low CO₂ concentrations during calcination results in a faster release of CO₂ and consequently higher overpressure stress for the particles and increased attrition. On the other hand low CO₂ partial pressure gives the benefit of less pronounced sintering. Finally humidity can also affect the hardness and elasticity of the material.

3.2 Thesis Statement

Calcium looping for CO₂ capture is a promising technology for the mitigation of CO₂ emissions in order to moderate climate change and global warming. This is due to benefits of this process presented earlier. This thesis aspires to contribute to the knowledge on the effect of water vapour on the process.

The effect of water vapour or commonly steam on the reaction of calcination and carbonation has not yet been fully understood. There is research conducted on the field but not sufficient, whereas often contradictive results can be noted. Moreover most research is conducted in small units such as TGAs and fewer on the scale of 10 kWth. However the effect of steam is of great importance since most fossil fuels contain a significant amount of water that can be found in the flue gases at a concentration of 5-10% [33]. This value can vary according to the type of fuel e.g. brown coal contains a far larger amount of water and this is why there are often drying units for this type of fuel before it is used for combustion. Presence of steam is expected in the carbonator as part of the flue gas coming from the power plant as well as in the regenerator since oxy-fired combustion of coal is proposed for the regeneration process. The study of the effect of water vapour should evolve primarily around the correlation of water vapour – steam presence and the efficiency achieved by the facility, which involves study of the effect on maximum carbonation and calcination conversion, as well as on the reaction rate of the sorbent. Additionally the effect on the sorbent properties should be studied, namely the mechanical and chemical properties. Finally the attrition rate in the presence of water vapour should be studied to determine the possible material loss and the respective make-up flow.

The thesis also aspires to contribute to the step of scaling up, since most of the studies conducted so far are on the level of thermo-gravimetric analysers (TGAs), as seen on the relative literature review earlier in this chapter. The study on the effect of water vapour in a 10KWth facility is essential for further scaling up to 200kWth and 1 MWth facilities, before industrial implementation. Conclusively the thesis aim would be to spherically address the matter, always in the framework of a diploma thesis since it copes with major scientific fields, in order to possibly become a useful tool in the further development of the technology in question.

4 Methodology and Experimental Procedure

4.1 Experimental Matrix

For the particular thesis a three set-up experimental plan was carried out. The outcome was tested for steam present in the carbonator and/or the regenerator. The experimental matrix is shown below in detail:

Table 4.1: Experimental Plan

	Regenerator			Carbonator		
Steady State	T (°C)	CO2inDRY (%)	H2Oin (%)	T (°C)	CO2inDRY (%)	H2Oin (%)
1	900	60	15	630	14	8
2	900	60	20	630	14	8
3	900	60	20	630	14	8
4	900	60	30	630	14	8
5	900	60	30	630	14	8
6	900	60	25	630	14	8
7	900	60	25	630	14	8
8	900	60	35	630	14	8
9	900	60	0	630	14	-
10	900	60	10	630	14	-
11	900	60	20	630	14	-
12	900	60	30	630	14	-
13	900	60	40	630	14	-
14	920	60	0	630	14	-
15	920	60	10	630	14	-
16	920	60	20	630	14	-
17	920	60	20	630	14	-
18	920	60	30	630	14	-
19	920	60	0	630	14	-
20	920	60	40	630	14	-

In particular the 1st experimental set-up was carried out with water vapour present in both the carbonator and the regenerator. The water vapour partial pressure in the carbonator was held steady, since the flue gas coming from the potential power plant is expected to have a fixed value of water vapour partial pressure depending on the type of coal used. The water vapour partial pressure in the regenerator varied in order to test the effect of various water vapour concentrations on the calcination process. The 2nd experimental set-up was carried out with various water vapour concentrations present in the regenerator only. Again the purpose of this set-up was to examine the effect of water vapour on the calcination process, but also to be compared with the 1st set in order to determine a possible effect of water vapour in the carbonator not only onto the carbonation but also to the calcination process as well. The 3rd experimental set-up was carried out with various water a different, elevated temperature. The purpose of this set-up was to determine the effect of water vapour concentrations in the regenerator only, but at a different, elevated temperature. The purpose of this set-up was

and possibly determine the dominant factor affecting calcination, or at which level water vapour affects the process in comparison to the temperature factor.

All three set-ups were also to be compared with previous experimental data for which no water vapour was involved, that derived from the facility during previous experimental campaigns. For the three set-ups in question all other parameters were kept relatively stable.

Flue gas composition (Typical Hardcoal)								
CO ₂	SO ₂	N ₂	H ₂ O _{d.a.}	H ₂ O _{h.a.}				
17.31%	0.05%	75.29%	7.31%	8.25%				

Table 4.2: Flue gas composition for typical hardcoal as per (d.a.-dry air, h.a.-humid air)

For the calculation of the respective water vapour partial pressures of the experimental set-ups, a typical coal composition as derived from [55] was utilized. In particular for the case of hardcoal the following flue gas composition occurs, under the assumption of stoichiometric combustion. The water vapour concentration is calculated in the table above for combustion with dry or humid air.

For the oxy-fired combustion of the same hardcoal in the regenerator a maximum water vapour partial pressure of 30% was calculated, if the CO_2 recirculation and the CO_2 release from the solids is not taken into account. The real H₂O concentration for this type of coal is expected to be less under actual conditions. Moreover a recycle of around 60% of the gas stream exiting the regenerator to achieve an equivalent 25% O₂ inlet concentration was assumed according to literature [9], leading to a concentration of around 55 to 65% CO_2 in the regenerator if high water vapour concentration is taken into account.

4.2 Description of Facility and Experimental Procedure

In the following figure a schematic of the facility in use is presented. The carbonator, the regenerator and the main components are depicted.



Figure 4.1: Facility Drawing

A thorough description of the facility can also be found elsewhere [6], as well as the relative hydrodynamic analysis [28].

The limestone used for the experiments of this thesis is a limestone originating from south Germany with the following chemical and structural properties:

 Table 4.3: Limestone utilized

Limestone									
CaO	SiO2	Al2O3	Fe2O3	MgO	Na2O	TiO2			
56.01	0.3	0.13	0.08	0.26	0.02	0.01			
Porosity (%)		Total pore	Mean pore	Bulk density	Apparent density				
		area (m²/g)	diameter	(g/ml)	(kg/ml)				
24.16		3.18	160	1.9	2.51				

To initiate the process the appropriate temperatures in the reactors have to be reached. The electrical heaters are switched on until they reach the respective temperatures. N type thermocouples were used along the reactors to measure the temperature at different spots. The MFC devices – Mass Flow Controllers are also switched on and tested to provide

the appropriate aeration to the regenerator, the carbonator and the two loop seals. The MFC devices have to be calibrated for adequate corrections of the resulting data.

Thereafter the reactors have to be filled with the appropriate amount of sorbent – precalcined lime, in order to achieve the respective circulating and bubbling fluidized bed conditions. The pressure drop profiles were provided by transducers allowing us to monitor the mass content of the reactors and the loop seals. Eventually stable circulation of the material is established. The latter is achieved in two steps: first stable internal circulation is achieved, which means that circulating fluidization conditions have been established in the carbonator. Thereafter the cone valve is opened and external circulation is also established. Now there is cyclic flow of the sorbent from the carbonator to the regenerator.

At this point and as long as the desired temperature, pressure and circulation rate have been reached, the CO_2 flow – FCO_2 is introduced in the carbonator. The lime - CaO captures CO_2 and leaves the reactor in a mixed form of CaO and CaCO₃. Together with the CO_2 lean flue gas stream it passes through the 1st cyclone of the carbonator. There, gas and solid are separated. The gas stream also containing fine particles goes through the 2nd cyclone of the carbonator, then through the candle filters and then part of it through the gas analyser, an ABB Advance Optima 2020 for this case, whereas the rest is released into the atmosphere. The 2nd cyclone and candle filters retain the fine particles from the gas stream.

The solids separated earlier in the 1st cyclone go through the standpipe and into the ULS. The ULS resembles a small FB, since it utilizes N₂ aeration to fluidize the solids. There part of the solids return to the carbonator and part of them to the regenerator. The amount of solids leaving the internal loop to enter the regenerator is determined by the cone valve. The CV is a novelty of this facility and is remotely operated from the control room. The material that goes through the CV then enters the regenerator. There it is calcined to the form of CaO again, whereas the CO₂ released leaves the reactor in a rich CO₂ stream. It passes a cyclone and a candle filter and part of it is measured by a gas analyser, an ABB Easy Line 3020 for this case, whereas the rest is released into the atmosphere. The regenerator has a bubbling bed and so the additional material that enters overflows to the LLS.

Finally the LabView software program is used to control the facility and acquire the respective data.

Steady state operation of the facility is achieved in order to take solid samples. Steady state is named here the condition of stability for a respectable amount of time, during which measurements can be taken, that can be considered representative of the result, regarding the respective experimental conditions. For the sets of experiments conducted during this thesis a period of 10 to 15 minutes was considered to be adequate. The parameters that are kept steady are the following: The mass in the carbonator, (in the regenerator it should be steady due to the overflow pipe), the fluidization velocity, the temperatures, the CO₂ concentrations especially in the regenerator since they directly affect the calcination process and the circulation rate and CO₂ flow in the carbonator. The circulation rate is measured by filling a pipe of known volume integrated in the facility. For the last two factors the looping ratio FCa/FCO₂ can be kept steady instead.

Solid samples are taken after each steady state, respective to the conditions of the carbonator and the regenerator. For the regenerator, samples were taken from the LLS, since the material accumulated there derives solely from the regenerator and is expected to provide us with the X_{calc} value needed, namely the carbonate content after calcination. For the carbonator, samples were taken from the ULS, since the material accumulated there derives solely from the carbonator, samples were taken from the ULS, since the material accumulated there derives solely from the carbonator and is expected to provide us with the X_{carb} value, namely the carbonate content after calcination.

4.3 Laboratory Analysis

The carbonate content of the samples collected was measured by a thermogravimetric analyser, in particular TGA 701 by LECO at the IFK laboratory. The sample was heated in order to dissipate any water it may contain at a low temperature. The initial mass as well as the mass of the sample after dehydration was measured. The sample was then heated at a high temperature for an amount of time adequate to be fully calcined. After that the sorbent left is purely CaO, since the CO₂ it contained was released during calcination. The final sample mass was measured. Comparing the final mass left to the mass after dehydration allows us to know the amount of CaCO₃ in the sorbent, namely X_{carb} .

A TG analyser developed by the IFK institute in cooperation with Linseis Thermal Analysis was also used to validate the Xcalc values from the TGA 701 and to calculate the maximum carbonation conversion - $X_{max,ave}$ value. The particular device showed a latent mass increase following the temperature increase. Summarily the samples of steady states taken from the LLS were heated up to 900°C in order to be fully calcined. From the mass difference the calcination conversion value - X_{calc} value was calculated. Then the temperature was lowered at 650°C and the samples were fully carbonated to determine the maximum carbonation conversion - $X_{max,ave}$. In the end a comparison of the results of the two devices took place.

The maximum carbonation conversion $X_{max,ave}$ of each sample was measured by the TG analyser developed by the IFK institute in cooperation with Linseis Thermal Analysis. The following diagram presents a typical carbonation curve. It is taken from an experimental steady state and is indicative of the various reaction areas. In the beginning of the reaction

the fast reaction regime can be noticed, during which a kinetic controlled reaction takes place. Most of the CO₂ is captured during this regime. Thereafter follows the slow reaction regime which is controlled by diffusion. It is suggested that during the fast reaction regime CO₂ is rapidly captured at the surface of the CaO grains forming a critical product layer [56]. After that point the carbonation reaction still takes place at a much slower pace. The CO₂ gradually enters the pores of the CaO grains due to diffusion to be captured.

The tangent of the fast reaction and that of the slow diffusion regime intersect at a point that gives the Xmax value. The $X_{max,ave}$ value is the maximum carbonation conversion of the sorbent in the fast reaction regime time, that is considered to be the carbonator reaction time for the Ca-looping process.





Additionally the particle size distribution of the sorbent - PSD was measured. A Malvern device was used for this purpose. The device calculates the dp10, dp50 and dp90 as well as the cumulative size of the sorbent using a laser beam. Finally the surface area of the sorbent and porosity of the sorbent were also measured utilizing the BET - Brunauer Emmett Teller method. In particular microstructure of sorbents was examined by means of Energy Dispersive-Scanning Electron Microscopy (EDS/SEM, 6300 JEOL; samples were coated with Au to reduce charging). Nitrogen adsorption measurements were performed using an Autosorb-1, Micropore version, static volumetric system (Quantachrome Instruments), at 77 K. Prior to each measurement the sorbents were outgassed overnight at 623 K under high vacuum.

4.4 Measured and Calculated Parameters

• **Circulation rate:** The optimal choice of the sorbent recirculation rate should be determined as a trade-off between the conflicting requirements of increasing the carbonation efficiency and decreasing the thermal power demand at the regenerator.

• **Residence time:** It is calculated based on the sorbent mass of the respective reactor and the circulation rate.

• **Space time:** It is defined as the ratio of molar inventory in the carbonator to the CO₂ inlet molar flow and expresses the bed inventory for a specific FCO₂. It is calculated based on the sorbent mass of the respective reactor and the CO₂ inlet flow.

$$au_{space} = rac{N_{Ca}}{F_{CO_2}}$$
 in min

- Active space time: It is defined as the product of space time and the free active CaO part bed. $\tau_{active} = \frac{N_{Ca}}{F_{CO_2}} * f_a * X_{max}$
- Looping ratio : It is calculated based in the circulation rate and the CO₂ inlet flow.

$$\mathbf{LR} = \frac{\mathbf{F}_{Ca}}{\mathbf{F}_{CO_2}}$$

• Gas inlet flows: The gas inlet flows are given by MFC controllers.

• **Gas outlet flows:** The gas outlet percentages are given by gas analysers. The CO₂ outlet percentage is measured, whereas corrections are applied that take into account possible air leakages, according to the O₂ found at the exit. Finally a N₂ measurement is utilized occasionally to calculate the outlet flow at the exit point.

Temperatures: Measured by type K thermocouples

• **Pressures and mass content:** The pressures along the reactor are measured by pressure transducers. The mass content is calculated by the respective pressure drop.

$$\Delta \mathbf{P} = \frac{\mathbf{W} \ast \mathbf{g}}{\mathbf{A}}$$

W is given in kg, ΔP in 100mbar, g is the acceleration of gravity c.a. 9.81 m/s² and A is the area of the reactor given by the equation $A = \frac{\pi^* D^2}{4}$ in m².

The pressure drop expected in order that the facility works normally is around 25mbar for Elwira, 70 to 100 mbar for Diva and around 80 mbar in the standpipe.

Mass balance:

The concept of the mass balance calculation is that the CO₂ captures in Diva should be equal to the CO₂ absorbed in the solids or the CO₂ that was released during calcination in Elwira.

$$F_{CO_2} * E_{carb} = F_{Ca} * (X_{carb} - X_{calc})$$

4 Methodology and Experimental Procedure

For Elwira the CO₂ measured should be equal to the CO₂ inlet plus the CO₂ released from solids: $CO_2^{measured} = CO_2^{inlet} + F_{Ca}(X_{carb} - X_{calc})$

• Efficiency of the carbonator: The efficiency of the carbonator refers to the amount of CO₂ that can be captured by the solids. It can be calculated by the CO₂ inlet and outlet flows.

$$\begin{split} E_{carb} \text{ or } E_{CO_2} &= \frac{Y_{CO2in} - Y_{CO2out}}{Y_{CO2in}} \\ E_{CO_2} &= n_{Ca}^{carb} * \frac{dx}{dt} \\ E_{carb} &= K * \Phi * X_{max} * T_{space} * f_a * (C_{CO2} - C_{eq}), \qquad f_a = 1 - exp(-\frac{t^*}{T_{res}}), \end{split}$$
[27]

K is a reaction speed factor, Φ contact factor, Xmax maximum conversion capacity, Tres the residence time in Diva, Cco₂ and Ceq the CO₂ and CO₂ equilibrium concentrations respectively and f_a the number of particles below t^{*}, within the fast reaction regime, able to react.

• Efficiency of the regenerator: The efficiency of the regenerator refers to the amount of CO₂ captured from the solids that can be released. It can be calculated from the CO₂ content of the solids leaving and entering the carbonator, Xcarb and Xcalc respectively.

$$\mathbf{E_{reg}} = \frac{\mathbf{Xcarb} - \mathbf{Xcalc}}{\mathbf{Xcarb}}$$

• CO2 equilibrium: [57] It is calculated based on the temperature of the carbonator.

$$CO_{2equil}(\%) = (4.137 * 10^7) * \exp\left(\frac{-20474}{(T_{carb} + 273.15)}\right) * 100$$
[56]

• Equilibrium carbonator efficiency: It is calculated based on the CO₂ equilibrium value and the CO₂ inlet and outlet concentrations.

$$\mathbf{E}_{\text{CO}_{2equil}} = \frac{\text{CO}_{2}^{\text{in}}(\%) - \text{CO}_{2equil}^{\text{out}}(\%)}{\text{CO}_{2}^{\text{in}} * (1 - \frac{\text{CO}_{2equil}^{\text{out}}}{100})} * 100$$

• **Theoretical cycles** [27]: The N_{th} expresses the amount of times that the moles of CO₂ captured could carbonate the bed inventory NCa up to its CO₂ carrying capacity $X_{max,ave}$.

$$N_{th} = \int \frac{E_{CO_2} * F_{CO_2}}{n_{Ca} * X_{max}} * dt$$

5 Results, Discussion and Conclusion

5.1 Quality of the Experimental Data

5.1.1 Steady States and Mass Balance

The steady states taken during the experimental procedure are presented below on the thermodynamic carbonation curve. Their respective CO_2 partial pressure and temperature is shown.



Thermodynamic Equilibrium Curve

Figure 5.1: Experimental Points - Steady States on the Thermodynamic Equilibrium Curve Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

The experimental data are validated through the closure of the mass balance equation:

$$\mathbf{F}_{CO_2} * \mathbf{E}_{carb} = \mathbf{F}_{Ca} * (\mathbf{X}_{carb} - \mathbf{X}_{calc})$$

The equation indicates that the CO₂ capture in the carbonator from the gas phase is found in the solid phase and should be released in the regenerator.

The following diagram presents the carbonator mass balance as shown in the following equation On the X axis there is the CO_2 moles per hour released from solids as

calculated by the X_{carb} and X_{calc} values of the TGA analysis. On the Y axis there is the CO₂ moles per hour captured as calculated from the gas analysers and MFCs. Eventually the two

different captured CO_2 calculations should be in agreement for all three experimental sets. It can be seen that this is the case for most points. The significant deviation of some points is mainly attributed to the uncertainty or errors of the carbon content that derived from the TGA analysis.



Figure 5.2: Carbonator Mass Balance **Exp. case 1: Carb:** 16% CO₂, 8% H₂O, rest N₂, 630°C **Reg:** wet flue gas, 46% CO₂, rest N₂, 900°C **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C **Exp. case 3: Carb:** 14% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 61% CO₂, rest N₂, 920°C

On the next diagram the mass balance for the regenerator is presented for the three experimental cases. On the X axis there is the regenerator CO_2 outlet flow in percentage as measured on the facility. On the Y axis there is the theoretically calculated CO_2 outlet considering the CO_2 entering the regenerator and the CO_2 released from solids. It can be seen that the two different CO_2 outlet estimations are in agreement. Again the main factor of deviation was the uncertainty and possible errors of the TGA analysis during the calculation of the CO_2 released by solids.







Figure 5.4: Example of Steady State for the Carbonator



Figure 5.5: Example of Steady State for the Regenerator

The two diagrams below are indicative of a steady state condition for the carbonator and the regenerator respectively. The 5th steady state of the second experimental set with steam in the regenerator at 900°C was chosen to be demonstrated, since it presented the steadiest measured values for both the carbonator and the regenerator.

For the carbonator the CO_2 inlet stream value should obviously be greater than the CO_2 outlet value, whereas the opposite applies for the regenerator. It is noticed that the CO_2 inlet and outlet streams, as well as the temperature remain stable for both reactors during the steady state.

It is noted that the CO_2 inlet and outlet values for both reactors are close which is indicative of low efficiency. However we should bear in mind that the experimental efforts of this thesis were mainly focused in determining the effect of water vapour presence. Other factors that greatly affect the efficiency such as solid circulation rate were not necessarily optimized.

5.2 Maximum Carbonation Conversion of the Sorbent (X_{max,ave})

In the following diagrams the maximum carbonation conversion versus the cumulative moles of H_2O/mol Ca and versus the correspondent water vapour partial pressures can be observed for the 1st experimental case, with water vapour in both reactors. The maximum carbonation conversion is the value of the capture capacity of the sorbent; high $X_{max,ave}$ is also related to higher efficiency of the carbonator according to the E_{carb} equation. The variable of cumulative moles of H_2O/mol Ca was chosen in order to be able to compare the different experimental cases, each of which has undergone different sintering due to different amounts of water vapour that have been through the reactor. The initial Xmax value of the fresh material for this experimental case drops rapidly at first, following the sorbent decay trend found in literature [20], until it reaches a relatively stable value around 20%. In conclusion the sorbent gradually loses the ability to capture CO₂, however for this case the sorbent activity remains at high levels in comparison to previous experiments without steam.

By observing the diagram of water vapour partial pressure it is noted that initially the X_{max} value remains constant for an increase of 10% H₂O partial pressure. For a stable value of 20% partial pressure the X_{max} value drops. For a further 10% H₂O increase the X_{max} value remains constant if not slightly improved. Again for a stable value of 30% partial pressure the Xmax value drops. The same tendency is observed also for the last two steady states. The above is indicative of a possible temporary enhancing effect of increased water vapour partial pressure, that decays over time as would be expected for conditions without water vapour found in [20].



Figure 5.6: a)Maximum Carbonation Conversion versus cumulative H₂O/Ca b)Maximum Carbonation Conversion versus H₂O partial pressure **Exp. case 1: Carb:** 16% CO₂, 8% H₂O, rest N₂, 630°C **Reg:** wet flue gas, 46% CO₂, rest N₂, 900°C

In the following diagrams the maximum carbonation conversion versus the cumulative moles of H₂O/mol Ca can be observed for the experimental cases when water vapour was present only during calcination. For the 2nd experimental case –water vapour in the regenerator at 900°C the initial X_{max,ave} value of the fresh material drops rapidly at first until it reaches a relatively stable value of residual activity, following the sorbent decay trend found in literature [45]. Half of this material was used for the 3rd experimental case along with fresh material added to reach the total essential sorbent content. As a result the 3rd experimental case – water vapour in the regenerator at 920°C does not present the initial rapid decrease observed for the 2nd case. The overall maximum carbonation conversion tends to reach a stable value of 22 to 25%. Although for the 2nd case the residual point has not yet been reached it is presumed it would not reach values lower than these of the 3rd case. This is because 3rd case is correspondent to increased sintering due to the greater working time and higher temperature in the regenerator - 920°C. Finally the peaks observed in the diagrams are attributed to the addition of small batches fresh material to maintain the desirable sorbent circulation rate.



Figure 5.7: Maximum Carbonation Conversion versus cumulative H₂O/Ca
a) Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C
b) Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

Comparison of the Different Experimental Data

In the following diagram the maximum carbonation conversion versus the correspondent water vapour partial pressures can be observed for the three experimental cases, described in the caption. The variable of H₂O partial pressure was chosen in order to study a possible effect of the different water vapour environment for each particular steady state, in addition to the overall cumulative H₂O effect studied previously. The expected decay trend is observed [45] and although greater residual activity is achieved, high water vapour partial pressures do not seem to significantly affect the outcome.



Figure 5.8: The effect of water vapour partial pressure on $X_{max,ave}$ Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

In the following diagrams the maximum carbonation conversion versus the theoretical cycles and versus the experimental time (CO_2 present in the carbonator) can be observed for the three experimental cases, described in the caption. Additionally the experimental cases are compared to previous experimental data also described in the caption. The overall theoretical cycles and the experimental time variables were chosen in order to be able to compare the different experimental cases, each of which has undergone different sintering, since CO₂ captured and released is a major factor contributing to the sintering of the sorbent. Moreover the experimental time is a good indication of the decay of the sorbent activity. Both the theoretical cycles and the experimental time are a good norm for comparing with previous experimental data without presence of water vapour. It is observed that the sorbent activity presents a sharp initial degradation as expected [45] and reaches a rather stable level of residual activity. However for the experimental cases that water vapour is involved the residual activity level is around 20 to 23%, whereas for previous experiments that no water vapour was involved the residual activity level is lower, around 12%. The latter conclusion is of great importance since an increased capture capacity of the sorbent for many hours of operation means greater efficiency for a lower looping ratio value, probably less make-up flow and generally greater feasibility of the process in guestion. The following equation shows the relation between $X_{max,ave}$ and the E_{carb} [27]:

$$\mathbf{E}_{carb} = \mathbf{K} * \mathbf{\Phi} * \mathbf{X}_{max} * \mathbf{\tau}_{space} * \mathbf{f}_{a} * (\mathbf{C}_{CO2} - \mathbf{C}_{eq})$$

Increased maximum carbonation conversion around double like it was observed during this thesis, is to be found also in literature [33]. When water vapour is present during carbonation only, the finer pores are retained and the higher conversion is owing to a reduction in the diffusion resistance through the carbonate later. When water vapour present during calcination only there is a shift toward larger pores due to enhanced sintering. These pores are less susceptible to pore blockage thus allowing for the higher conversion. A synergistic effect of the above two properties was also observed for water vapour present in both the carbonator and the regenerator.



Figure 5.9: Maximum Carbonation Conversion versus Theoretical Cycles Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C Prev. experiments: Carb: 12% CO₂, rest N₂,630°C Reg: dry flue gas, 53% CO₂, rest N₂, 900°C [58]



Figure 5.10: Maximum Carbonation Conversion versus experimental time Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C Prev. experiments: Carb: 12% CO₂, rest N₂,630°C Reg: dry flue gas, 53% CO₂, rest N₂, 900°C [58]

5.3 Surface Area of the Sorbent

Surface area is related with the reactivity of the sorbent. Increased surface area offers more places for CO₂ to be captured on the surface of the particle during the fast reaction regime. The CO₂ capture continues thereafter through a slow diffusion mechanism. The development of the surface area of the sorbent for the experimental sets of this thesis is presented in the diagrams below.

The initial surface area of the sorbent is **7.98m²/g** for the fresh calcined material of the 1st experimental set and **6.22m²/g** for the 2nd experimental set. After 6hours and 30min the surface area has declined to **1.73m²/g** for the 1st experimental set and after 3hours 45min to **3.01m²/g** for the 2nd experimental set. The lower value for the 1st set is expected since the material has undergone cyclic carbonation/calcination for more time, thus presenting increased sintering and less surface area. For the 3rd experimental set half older material was used that had already undergone sintering and half fresh calcined material was added.





Figure 5.11: Surface Area

Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

In the following table the normalized surface area is presented for different experimental conditions. It is noted that when water vapour is present there is increased sintering as expected from literature [50] and greater decrease of the surface area. On the contrary conditions of previous experiments without water vapour presence present a rather stable value of normalized surface area that is maintained for several theoretical cycles. The increased maximum carbonation conversion reported earlier despite the greater decrease of surface area is also found in literature. Florin et al [33] suggested that although in the presence of water vapour during calcination a reduction in surface area is observed, there is also a shift to larger pores that are less susceptible to pore blockage, thus allowing for the higher conversion.



Figure 5.12: Surface Area Decrease Rate $S_{final}/S_{original}$ Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C Prev. experiments: Carb: 12% CO₂, rest N₂,630°C Reg: dry flue gas, 53% CO₂, rest N₂, 900°C [58]

The following two diagrams present the above samples in relation to the total water vapour and CO₂ corresponding to each sample. From the comparison of the trend lines of the two diagrams we can assume that CO₂ presence increases the sintering far more than H₂O presence since the respective trend lines are more inclined. In general we should expect that CO₂, H₂O and high temperatures promote sintering according to Borgwardt et al [50].



◆ Experimental case 1 ● Experimental case 2 ○ Experimental case 3 ◆ Experimental case 1 ● Experimental case 2 ○ Experimental case 3

Figure 5.13: a)Surface Area versus cumulative H_2O/Ca b)Surface Area versus cumulative CO_2/Ca Exp. case 1: Carb: 16% CO_2 , 8% H_2O , rest N_2 , 630°C Reg: wet flue gas, 46% CO_2 , rest N_2 , 900°C Exp. case 2: Carb: 10% CO_2 , rest N_2 , 630°C Reg: wet flue gas, 55% CO_2 , rest N_2 , 900°C Exp. case 3: Carb: 14% CO_2 , rest N_2 , 630°C Reg: wet flue gas, 61% CO_2 , rest N_2 , 920°C

5.4 Carbonator Performance

Carbonate Content of the Sorbent Exiting the Carbonator (X_{carb})

The X_{carb} value is the CaCO₃ formed when CaO captures CaO per moles of Ca. In the following diagram the carbonation conversion versus the residence time of the sorbent in the carbonator is plotted for the three experimental cases described in the caption. Xcarb value is of interest since according to the fundamental equation:

$$\mathbf{Ecarb} * \mathbf{F_{CO_2}^{in}} = \mathbf{F_{Ca}} * (\mathbf{X_{carb}} - \mathbf{X_{calc}})$$

it directly affects the efficiency of the carbonator; the higher the X_{carb} value the greater the CO_2 capture efficiency. It is observed that for similar residence time values, in particular between 4 to 8 minutes, the X_{carb} values for the 2nd and 3rd cases with water vapour in the regenerator is around 10 to 15%. A clear improvement is observed for the 1st case with water vapour in both reactors, that presents X_{carb} values of around 49%. It is also observed that points with great residence time present low X_{carb} values, contrary to what would be expected. For these points this is explained by great respective looping ratio values as it is presented later.

The experimental points are correspondent to various water vapour partial pressures in the regenerator. H₂O concentrations varied from 10 to 40%. However no significant changes or particular trends were observed. It is concluded that water vapour affected the Xcarb value only when present in the carbonator. The improvement in the reaction speed for this case can be found in literature [31], [32], [43], [44], [51]. Although its mechanism is not completely understood it is proposed that it is due to an improvement in heat transfer properties, since steam presents better heat transfer than CO₂ or air and/or an improvement in the porosity properties of the sorbent.



Figure 5.14: Xcarb versus residence time of the carbonator **Exp. case 1: Carb:** 16% CO₂, 8% H₂O, rest N₂, 630°C **Reg:** wet flue gas, 46% CO₂, rest N₂, 900°C **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C **Exp. case 3: Carb:** 14% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 61% CO₂, rest N₂, 920°C

Efficiency of the Carbonator (E_{carb})

The effect of steam partial pressure on the efficiency of the carbonator is studied here. Whether steam in different partial pressures in the regenerator or stable in the carbonator, in relation to other factors such as temperature, would improve the carbonation process. The carbonator efficiency is calculated by the following equation:



Figure 5.15: Carbonator Schematic

In the following diagram the efficiency of the carbonator versus the looping ratio is plotted for the three experimental cases described in the caption. It is observed that E_{carb} is an increasing function of looping ratio FCa/FCO₂. Moreover higher temperature gives higher E_{carb} values, since lower X_{calc} values are achieved, according to the fundamental equation:

$$\mathbf{E_{carb}} * \mathbf{F_{CO_2}^{in}} = \mathbf{F_{Ca}} * (\mathbf{X_{carb}} - \mathbf{X_{calc}})$$

Water vapour in the carbonator results to increased carbonator efficiency for the same looping ratio values, due to the increased reaction speed, according to the equation:

$$\mathbf{E}_{\mathbf{CO}_2} = \mathbf{n}_{\mathbf{Ca}}^{\mathbf{carb}} * \frac{\mathbf{dx}}{\mathbf{dt}}$$

The effect of water vapour in the carbonator and higher temperature appears to be stronger than the space time, since it can be seen that the 2nd case with the highest space time presents the lowest efficiencies in comparison to those of the 1st and 3rd experimental case that have lower space time values. According to the diagram for the 1st case with water vapour in both reactors great efficiency values are achieved for very low looping ratio values in comparison to the other cases. In particular for a looping ration of only 3, an efficiency of around 80% was achieved. This is a very optimistic finding since low looping ratios are desirable. High looping ratios mean increased heat losses due to the increased circulation of solids.



Figure 5.16: Carbonator efficiency versus looping ratio and space time Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

Carbonation Model Validation

Charitos et al [27] proposed a model that connects the efficiency of the carbonator to the active space time. According to the model a single equation can be used to design the process. The equation of active space time was used in order to describe the fact that only a fraction f_a of the total particle population is able to react and capture CO_2 . The model equations are the following:

$$\begin{split} & \text{Ecarb} = \text{Ks} \ast \Phi \ast X_{max} \ast \frac{N_{Ca}}{F_{CO2}} \ast f_a \ast \left(C_{CO2} - C_{eq} \right) \\ & \tau_{active} = \frac{N_{Ca}}{F_{CO_2}} \ast f_a \ast X_{max} \quad , \qquad f_a = 1 - \exp(-\frac{t^*}{T_{res}}) \\ & t^* = \frac{X_{max} - X_{calc}}{K_s \ast X_{max} \ast (\overline{C_{CO_2}} - C_{CO_2equil})} \quad , \qquad \overline{C_{CO_2}} = \frac{CO_{2in} - CO_{2out}}{\ln(\frac{CO_{2in}}{CO_{2out}})} \end{split}$$

Fitting the experimental data to the theoretical model provided the apparent kinetic constant for the particular experimental cases of this thesis. The highest kinetic constant is observed for the 1st experimental case with water vapour in both reactors equal to 2s⁻¹. The 2nd case with water vapour in the regenerator at 900°C presented the lowest apparent kinetic constant value 0.323s⁻¹, still higher than the value of previous experiments without water vapour around 0.26s⁻¹. The 3rd case with water vapour in the regenerator at 920°C also presented an increased value of 0.78s⁻¹.

For the fitting constant reported above good agreement was found between the experimental data and model calculations. The following diagram presents the experimental versus the model carbonator efficiency. Good agreement of the experimental data and the theoretical calculations can be observed.

Carbonation model validation



Figure 5.17: Experimental carbonator efficiency versus model carbonator efficiency Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

In the following diagram the experimental efficiency of the carbonator is plotted versus the active space time. On the diagram the model lines that occurred from the theoretical calculation can also be observed for each case. Again good agreement is observed between the experimental data and the respective model lines. It can be observed that especially for the 1st case with water vapour in both reactors for a very low value of T_{active} very high E_{carb} values are achieved. In particular 60% efficiency is achieved for this case with an active space time of less than 5sec, whereas for the 2nd case and for previous experiments without water vapour more than 30sec were needed for the same efficiency. Lower T_{active} values are correspondent to greater feasibility for the process.



Figure 5.18: Carbonator efficiency versus active space time **Exp. case 1: Carb:** 16% CO₂, 8% H₂O, rest N₂, 630°C **Reg:** wet flue gas, 46% CO₂, rest N₂, 900°C **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C **Exp. case 3: Carb:** 14% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 61% CO₂, rest N₂, 920°C

Increased carbonation reaction when water vapour is present during carbonation is also found in literature [33]. Florin et al suggested that in this case the reaction proceeds more rapidly in the initial stages of the reaction and the maximum reaction rate is higher compared to experiments without water vapour present.

5.5 Regenerator Performance

Carbonate Content of the Sorbent Exiting the Regenerator (X_{calc})

Due to the fact that our regenerator is a BFB and that high CO_2 partial pressures of up to 65% are to be found in the regenerator, some of the CO_2 carried from the sorbent in the form of $CaCO_3$ into the regenerator cannot be released, thus not all of the $CaCO_3$ is decom-

posed to form CaO when leaving the regenerator. The remaining $CaCO_3$ per mol Ca is the X_{calc} value.

The following diagram depicts the conversion of CaCO₃ to CaO (1-X_{calc}) for the different water vapour partial pressures and the respective regenerator residence time for the three experimental cases as described in the caption. From the 2nd and 3rd case with water vapour only in the regenerator, it is obvious that for similar residence times the conversion of CaCO₃ to CaO is an increasing function of water vapour partial pressure. The 1st case with water vapour in both reactors presents a relatively stable conversion independently of the water vapour concentration. This is explained by the high residence times of this case. It is assumed that the reaction has reached its limits. The sorbent has stayed long enough in the reactor and fraction that was able has already been conversed to lime. Mainly facility limitations due to the maximum heat transfer capacity do not allow for full sorbent calcination. The 3rd case presents high conversion values for the same residence time and water vapour concentration as the 2nd case due to the increased temperature that enhances calcination according to the thermodynamic equilibrium curve [30]. It also presents higher conversion values than the 1st case. This indicates that higher temperature increases the conversion limits as expected [30]. The enhancement of the calcination reaction found during this thesis is also consistent with the findings of Wang et al [44], who attributed it to the better thermal conductivity of water vapour than that of N₂.



Figure 5.19: Conversion of CaCO₃ to CaO versus water vapour partial pressure Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

In the following diagram the conversion of $CaCO_3$ to $CaO (1-X_{calc})$ is presented for the respective cumulative H₂O moles/moles Ca, for the three experimental cases as described in the caption. The tendency described above is validated, whereas the calcination limitations

independently of water vapour can also be observed. In conclusion although water vapour appears to enhance the calcination reaction, the factor of temperature seems to be the decisive one.



Figure 5.20: Conversion of CaCO₃ to CaO versus cumulative moles of H_2O/mol Ca Exp. case 1: Carb: 16% CO₂, 8% H_2O , rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

Efficiency of the Regenerator (E_{reg})

The effect of water vapour partial pressure on the efficiency of the regenerator is studied here. Whether steam either in the regenerator or the carbonator, in relation to other factors such as temperature, would improve the regeneration process. The regenerator efficiency (E_{reg}) is a function of the percentage of CO₂ in the sorbent (X_{carb}) that enters the regenerator in the form of CaCO₃ and of the percentage of CO₂ in the sorbent that could not be released during the calcination (X_{calc}) and leaves the regenerator still in the form of CaCO₃.

$$Ereg = \frac{Xcarb - Xcalc}{Xcarb}$$

It is obvious that a relatively good, namely low value of X_{calc} would affect the efficiency of the regenerator positively, since it would give a greater difference of $X_{carb}-X_{calc}$ and therefore a greater E_{reg} value. On the other hand things are not so simple regarding the X_{carb} . A relatively good, namely high value of X_{carb} would give a greater difference of $X_{carb}-X_{calc}$, however it would also give a greater denominator that would tend to decrease the Ereg value.

In the following diagram the efficiency of the regenerator is plotted against the value of $t_{res,reg}/X_{carb}$ in order to normalize and therefore compare the various experimental results.

The residence time affects the E_{reg} since the more time the sorbent spends in the bubbling fluidized bed of the regenerator the greater the portion of CaCO₃ that can be calcined. On the other hand a high value of X_{carb} in the sorbent entering the regenerator, would mean a greater load for the regenerator to calcine. In general increased efficiency is observed for an increasing $t_{res,reg}/X_{carb}$ ratio for all of the experimental cases. However some cases present a sharper increase than others. Moreover the 1st and 3rd experimental cases present higher efficiencies than the 2nd case and the previous experimental data without water vapour involved. For the 1st case this is attributed to the water vapour presence in both reactors that resulted in higher X_{carb} values, whereas for the 3rd case to the increased temperature that resulted in lower X_{calc} values. For these two cases it can be observed that E_{Reg} values as high as 90% were achieved for only 50s of regenerator space time. For the same space time E_{Reg} values of only 60% are achieved for the 2nd case and for previous experiments without water vapour involved. Lower space time leads to less sorbent needed and therefore to a smaller and more feasible reactor.



Figure 5.21: Regenerator efficiency versus regenerator load Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C Prev. experiments: Carb: 12% CO₂, rest N₂,630°C Reg: dry flue gas, 53% CO₂, rest N₂, 900°C [58]

The conclusion drawn by the 1st experimental case is that with the presence of water vapour in the carbonator, we can achieve increased efficiency for the regenerator. However a greater residence time–t_{res} in the regenerator is required, so that the increased Xcarb load is handled. This would postulate a larger regenerator, thus increased cost of construction and operation. In addition we should consider that for our experiments we used an electrically heated BFB as the regenerator, whereas for the upscaling an oxy-fuel CFB combustor will

be used, which presents a set of advantages mentioned earlier in this thesis. Alternatively we would have to operate the regenerator at a higher temperature, thus we would have an increased demand for heating energy and therefore increased cost of operation. Therefore to estimate the greater overall efficiency of the facility-potential power plant, a feasibility study should be conducted to determine the best of the alternative options.

Moreover the achieved efficiencies of around 90% are quite satisfactory for the particular facility and operation conditions, regarding the BFB type of the regenerator as well as the fluidization velocity.

5.6 Comminution Phenomena

In this chapter the attrition of the sorbent is studied, especially under the effect of steam. The attrition rate of the sorbent is a major factor concerning the design of the facility and the selection of limestone, since high attrition rate would consequently mean greater make up flow of sorbent, thus increased cost of operation. Therefore the appropriate kind of limestone should be selected presenting high attrition resistance, in accordance to the operational conditions of the facility. Moreover appropriate cyclones should be selected that would allow only the finer particles to leave the looping cycle, without developing high velocity of the exhaust gas that would lead to increased attrition, also properly designed to avoid blockage from possibly agglomerated particles.

The influence of main operating variables, namely superficial gas velocity, mass and particle size of the sorbent on fines generation has been investigated and experimental results have confirmed the validity of the relation [52]:

$\mathbf{E} = \mathbf{k}(\mathbf{U} - \mathbf{U}_{mf})\mathbf{m}/\mathbf{d}$

U is the fluidization gas velocity, U_{mf} the minimum fluidization gas velocity, m the mass and d the particle diameter. k is a suitable constant. According to this equation the higher the fluidization velocity the greater the attrition rate. This relation has already been proposed and extensively applied to the attrition of carbon during the fluidized bed combustion of coals [52].

To calculate the attrition rate of the sorbent the make-up batches added to the system to compensate for material losses had to be calculated. After consulting the experimental records we were able to sum up the small batches of extra sorbent that were added in the looping cycle, each around one to two kilos, in order to maintain the steady operation of the facility and also a relatively stable circulation rate of the sorbent. The material loss was attributed solely to the disintegration of the sorbent due to attrition and the consequent abduction by the gas stream through the cyclone and out of the system. Therefore the make-up batches are expected to be almost equivalent to the flow of material exiting the system through the cyclone. Afterwards the overall material in kg added, was divided by the total mass of the system and then divided by the overall working hours of the facility, providing the value of wt(%)/h, the percentage of mass loss per hour.

As stated previously in the theoretical part of this thesis the attrition rate is mainly dependent on the following factors: operating temperature, steam partial pressure, fluidization gas velocity and CO₂ partial pressure.

The following diagram depicts the attrition rate for four different sets of experiments. On the Y-axis the attrition rate is presented in weight percentage of the sorbent per hour, whereas on the X axis the four different sets of experiments. The first was conducted during previous experimental work in the facility and did not involve steam presence in either the carbonator or the regenerator. The other three were performed during the present diploma thesis and involved sequentially steam in both the carbonator and regenerator at 900°C and steam only in the regenerator at 900°C and 920°C respectively. For the set conducted during previous experimental campaigns the fluidization velocities, CO₂ partial pressures and temperatures were more or less similar to the present ones. Moreover the same limestone was used in all cases with the respective properties presented earlier in this thesis.



Figure 5.22: Mass loss per hour for different experimental conditions Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C Prev. experiments: Carb: 12% CO₂, rest N₂,630°C Reg: dry flue gas, 53% CO₂, rest N₂, 900°C [58]

It is noted that the experimental sets with steam only in the regenerator at a temperature of 900°C and 920°C present a significantly higher attrition rate **2.12** and **2.25%** respectively in comparison to the **0.8%** estimated for the previously conducted experiments with no steam at all. This higher value is attributed to softening mechanisms of the sorbent, occurring due to the presence of steam in the regenerator. The last (3^{rd}) experimental set conducted at a temperature of 920°C in the regenerator presents a lower attrition rate possibly due to the hardening of the material related to the increased temperature, as well as due to the partial utilization of older material already to have reached a decreased residual attrition rate [52], [48], since attrition is initially greater and gradually decays into a steady value. The last (3^{rd}) set was overall correspondent to a significantly greater cumulative H₂O load of 203 moles, in comparison to that of the previous (2^{nd}) set, around 88 moles. It appears that the effect of increased temperature is important for the 3^{rd} case, which presented decreased rate of attrition. This assumption is supported by the fact that the 3^{rd} case is correspondent to less Ca/CO₂ make-up flow than the 2^{nd} case, as it is presented in the next diagram. However the partial utilization of old material should also be taken into consideration, that should present less initial attrition but also smaller initial size.

In the following diagram the attrition for different experimental conditions is plotted again. On Y-axis the make-up flow F₀ per the overall moles of the carbonator CO₂ inlet can be found, in order to provide useful data for the application in other facilities and the scale-up of the process. Practically the diagram shows how many moles of Ca are needed in the system for each mol of CO₂ captured.



Figure 5.23: Material loss per CO₂ moles for different experimental conditions Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C Prev. experiments: Carb: 12% CO₂, rest N₂,630°C Reg: dry flue gas, 53% CO₂, rest N₂, 900°C [58]

Moreover in the following diagram the attrition normalized by the respective circulation rate of the sorbent is presented for the various experimental conditions. Again this diagram is presented in order to provide useful data for the application in other facilities and the scale-up of the process.



Figure 5.24: Attrition expressed in make-up flow per circulation rate Fo/Fca Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C Prev. experiments: Carb: 12% CO₂, rest N₂,630°C Reg: dry flue gas, 53% CO₂, rest N₂, 900°C [58]

In general it is be observed that the higher attrition rates were noted for the experimental case with steam in both carbonator and regenerator, approximately **4.8%/h**, more than double for the days with steam only in the regenerator. This extremely high value is attributed to softening mechanisms of the sorbent, occurring due to the presence of steam, as mentioned previously. It also appears that the combined presence of steam in both carbonator and regenerator greatly worsens the attrition rate compared to the sets with steam only in the regenerator. The softening mechanisms presumed lead to increased fragmentation and smaller particle size.

Additionally for the 1st case with water vapour in both reactors a series of operating difficulties were noted, such as 'cement' formations that blocked the 1st cyclone of the carbonator, inhibiting the stable flow of material in the secondary loop and resulting to the accumulation of active sorbent in the 2nd cyclone of the carbonator, out of the system. The formation of these blockages mainly in the piping after the carbonator reactor, could be attributed to the lower temperature of the carbonator (630°C) which in correlation to the lower temperatures at the pipes and the cyclones of the carbonator could lead to the existence of cold spots. These cold spots for example in the 1st cyclone in combination to the steam presence could lead to the agglomeration of particles, at first forming small rigid agglomerates, subsequently larger 'cement' blockages due to the continual deposition of particles. Also small flat

pieces, larger than the normal sorbent particles were observed in the sample taken from the bed of the carbonator at the end of the 1st experimental set.

The following photographs are of samples taken the day following the 1st experimental case, during maintenance of the facility and support the observation of the 'cement' formations. It is noted that the one side of a 'cement' block sample taken from the 2nd cyclone of the carbonator, appears to be smooth, probably since the block was attached on the surface of the pipe or cyclone. The other side presents a rough corrugated surface, probably due to the continual deposition of particles as they passed along that point.



Figure 5.25: a)'Cement' formation side one

b)'Cement' formation side two

It is noted that similar 'cement' formations were noted in the piping after the regenerator for this 1st set, despite the higher temperature of the regenerator (900°C). These formations were not as rigid; they were rather fragile and fell easily apart. Also they consisted of very fine, elutriated particles, which is expected since the regenerator is a bubbling fluidized bed with consequent small fluidization velocities that would not be able to lift heavier particles. Presumably these formations occurred only after the end of the experiments when the facility was shut and the temperature dropped, at which time the sample was taken. The fact that no blockage in the cyclone of the regenerator was observed during the operation is in agreement with the above.

Particle Size Distribution

In this chapter the particle size distribution of the sorbent is studied. PSD is an important factor affecting the calcium looping process, since the smaller the particles the greater the chance that they leave the system through the cyclone resulting to a larger necessary amount of make-up flow. On the other hand smaller particles present in total greater surface area for the same amount of mass, able to react and capture or release CO₂ in the carbonator or the regenerator respectively.

The diagram that can be firstly drawn to present the range and magnitude of the particles size in our facility is the following. PSD is presented here for the raw calcined limestone–CaO, for the material of the carbonator bed and for the circulating material taken from the ULS at the end of the 1st experimental case. These samples presented a dp₅₀ value of **382µm**, **605µm** and **354µm** respectively. The material of the carbonator bed presents as expected the largest particles to be found in the system, since it is a CFB reactor utilizing high fluidization velocities that lift all relatively light particles and lead them through the cyclones. The particles to be found in the bed mass are therefore expected to be the larger heavier ones after some time of facility operation.



Figure 5.26: Particle size for raw limestone, carbonator bed and circulating sorbent

The diagram below presents the particle size for the raw uncalcined limestone– CaCO₃ in comparison to the calcined raw calcium oxide–CaO of two different experimental sets. As expected the limestone presents similar particle size with the newly calcined material, since no time was given to the attrition mechanisms to act. Moreover the regenerator reactor is a BFB bed that utilizes low fluidization gas velocities, thus the minor initial attrition. Still the dp₅₀ particle size of raw limestone is **413µm**, greater of the calcined material dp₅₀ particle size of **382µm** and **395µm** for the two sets.


Figure 5.27: Particle size for EnBW limestone and two raw calcined material samples **Exp. case 1: Carb:** 16% CO₂, 8% H₂O, rest N₂, 630°C **Reg:** wet flue gas, 46% CO₂, rest N₂, 900°C **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C

The following diagram depicts the material particle size of the bed of the carbonator and regenerator in comparison to that of the circulating material taken from the ULS at the end of the 2nd experimental case. The results are consistent with the previous conclusion that the heaviest, largest particles accumulate in the carbonator bed. Moreover it can be observed that the material of the bed of the regenerator has lower value of dp₅₀ particle size in comparison to the carbonator bed, since it is a BFB utilizing lower fluidization gas velocities.



Figure 5.28: Particle size for raw calcined material, carbonator and regenerator bed **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C

The following diagram presents the particle size of the regenerator bed material for the three different experimental cases, as well as the calcined raw material for better comparison. The particle size is similar for all three cases. However a difference can be noticed for the 2nd case with water vapour in the regenerator at 900°C that presents a dp₅₀ value of 430µm in comparison to that of around 400µm for the other two sets. It is presumed that the particle size follows the attrition trends observed in the previous chapter. So the smaller particle size for the 1st and 3rd case could be attributed to the far greater total amount of steam for these sets. This could be the case even for the 3rd set held at a higher regenerator temperature that should normally cause hardened material, more resistant to attrition. However for this last set the partial utilization of older material from the previous set probably gave already smaller particles from the beginning of the experimental set, so no safe conclusion can be drawn. The calcined raw material although it presents a dp₅₀ of 395µm, similar to the 1st and 3rd case, it also presents a different, more even distribution. The material is at the initial stages of attrition due to the BFB regenerator and also it has not been looping through the carbonator, thus larger particles that have not undergone fragmentation can be observed, as well as smaller particles that have not yet been captured by the cyclone.

> **Regenerator Bed** 12 Experimental case 1 **Experimental case 2** 10 Experimental case 3 oarticles in (%) ·· Calcined raw 8 6 4 2 0 200 400 600 800 1000 1200 0 size (µm)

Figure 5.29: Particle size of the regenerator bed for three different experimental cases Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

In addition to the above diagrams the following pictures are cited, presenting the raw limestone, the calcined raw material and the material from the bed of the regenerator after many hours of operation. As it can be observed even after the first calcination the material has already undergone significant attrition, probably mainly due to abrasion as proposed for a BFB regenerator [52], that has changed its initial surface removing very fine particles at-

tached. After many hours of operation the particles appear to have a smoother surface and be more spherical, as expected due to the abrasion and rounding off during the continuous calcium looping cycles.



Figure 5.30: a)Raw limestone EnBW

b)Calcined raw material



Figure 5.31: Regenerator bed

The following diagram presents the dp_{50} size for the following conditions: calcined raw material, water vapour in both carbonator and regenerator, water vapour only in the regenerator at 900°C and 920°C respectively and no water vapour. All samples except the calcined raw were taken at the end of each experimental case. The last sample-no water vapour refers to older experiments held in the facility with no steam and a variety of CO₂ partial pressure values, but with the same type of limestone. The circulation of material alone can cause attrition due to abrasion and collisions, so the overall working time is presented in the diagram. The 2nd case presents the highest attrition of the cases of this thesis since it is correspondent to the highest relative attrition, here it presents greater dp₅₀ value due to the less working time in the facility-8hours. Finally the 3rd case corresponds to the highest working time. The high dp₅₀ value indicates low attrition perhaps due to hardening mechanisms

that can be attributed to the increased temperature. However half of the material for this case was new leaving a margin of error for this assumption. The calcined raw material naturally presents the highest size of all, since it has not undergone significant attrition.



Figure 5.32: Median value of particle size – dp₅₀

Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C Prev. experiments: Carb: 12% CO₂, rest N₂,630°C Reg: dry flue gas, 53% CO₂, rest N₂, 900°C [58]

The peculiarity of this diagram is the dp₅₀ particle size of the last, older case with water vapour at all that is clearly smaller, despite the fact that no significant attrition was observed for this case in comparison to the sets with steam. This finding is quite unexpected and could possibly be attributed to experimental errors due to the utilization of different measurement techniques and devices. However this sample from previous experiments with no water vapour refers to around 22 working hours in the facility, which could explain the significantly smaller particle size. Another possible explanation could be that for the sets that water vapour was involved, during the sampling procedure, part of the water vapour was taken along with the sorbent since there was significant steam partial pressure. As the sample cooled down the vapour could liquefy into water causing the formation of sorbent agglomerates. This is only a hypothesis, however the following photograph of a sample taken from the bed of the regenerator after cooling down at the end of an experimental set-up, possibly coincides with this conclusion.



Figure 5.33: Regenerator bed after an experimental set-up

The following table features the bulk density of the sorbent for the three experimental cases and for the initial raw limestone. The calculation of the bulk density is explained at the experimental part of this thesis. Smaller particles are expected to present higher bulk density. The particular table is not in consistency with the above findings of median particle size, since the samples used to measure the bulk density were taken around the middle of each experimental set-up in order to be representative. On the other hand the dp₅₀ values presented earlier correspond to samples taken at the end of the set-ups, thus correspondent to different attrition values.

Table 5.1: Bulk density of the sorbent

Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C **Reg:** wet flue gas, 46% CO₂, rest N₂, 900°C **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C **Exp. case 3: Carb:** 14% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 61% CO₂, rest N₂, 920°C

Bulk Density of the Sorbent (kg/m³)							
Raw Limestone	Experimental case 1	Experimental case 2	Experimental case 3				
1900	1348	1067	1076				

Furthermore several photographs from different samples taken along the experimental procedure are also included in the annex of this thesis, in order to better present the PSD results and the relative attrition mechanisms. The list of samples chosen for microscope photographs is also presented in the annex.

The following diagrams describe the development of dp₅₀ size during the different experimental sets:



Figure 5.34: Median value of particle size – ULS samples versus experimental time (CO₂ in the Carb) Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C Prev. experiments: Carb: 12% CO₂, rest N₂,630°C Reg: dry flue gas, 53% CO₂, rest N₂, 900°C [58]

The diagram depicts the median particle size value and the respective time for samples taken from the upper loop seal. The decrease of particle time as time advances is obvious. The 3^{rd} experimental set with steam in the regenerator at 920°C presents a rather stable particle size. This could be due to two factors. One is the partial use of older material from the 2^{nd} set with steam in the regenerator at 900°C. The older material has already undergone the initial increased attrition and has already reached the more stable condition of decreased attrition. Moreover this set was held at increased temperature that is supposed to further harden the material and render it less prone to attrition. The partial utilization of new material also explains the increase of dp50 value for the 3^{rd} set although this set is consecutive to the 2^{nd} set with steam in the regenerator at 900°C.

Another important observation is that although the initial dp50 value of raw limestone is **413µm** and of raw calcined material around **385µm**, the initial dp50 value of the ULS samples is 430-460µm. This is possibly explained by two reasons: The formation of agglomerates due to the drop of temperature and the existence of cold spots in the pipes leaving the carbonator and in the cyclone, in combination to the presence of water vapour. The other more likely one is that the cyclone has filtered the fine particles so only the particles above a certain size proceeded to the upper loop seal. The median value of these particles is of course expected to be higher than that of the calcined raw material or the raw limestone, since no fine particles are included.



Median value - Lower loop seal samples

Figure 5.35: Median value of particle size – LLS samples **Exp. case 1: Carb:** 16% CO₂, 8% H₂O, rest N₂, 630°C **Reg:** wet flue gas, 46% CO₂, rest N₂, 900°C **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C **Exp. case 3: Carb:** 14% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 61% CO₂, rest N₂, 920°C

This diagram presents the median particle size over time for samples derived from the lower loop seal. The strange tendency observed is that towards the ending of the experimental set the particles seem to have larger median particle values. An explanation about this could be again the presence of steam. Especially towards the end of the set there is very high steam partial pressure up to 35%. Possibly steam is also present in the overflow pipe leading to the lower loop seal. The decrease of temperature in the overflow pipe and the seal could lead to agglomerate formation. Another possible explanation for the first two sets at 900°C is the addition of make-up material during the last steady states. These kilos of fresh material would increase the overall particle size and therefore the median value. Finally finer particles are constantly filtered by the cyclones. At the beginning there is increased attrition that outweighs the filtering of fines and so the dp50 value seems to decrease. Towards the end maybe the attrition reaches a residual negligible value and therefore the filtering outweighs the attrition rate. All these factors may also have a synergistic effect.

6 Summary

In the framework of this diploma thesis the effect of water vapour on the Ca-looping process was experimentally investigated at a $10kW_{th}$ dual fluidized bed facility. The effect of water vapour was studied in terms of the sorbent mechanical and chemical properties, CO₂ capture efficiency of the carbonator and CO₂ release efficiency of the regenerator, material losses and the essential make-up flow of sorbent.

In summary three different experimental set-ups take place. The 1^{st} experimental case with stable water vapour in the carbonator and varying water vapour in the regenerator at 900°C. The 2^{nd} experimental case with varying water vapour in the regenerator at 900°C and the 3^{rd} experimental case with varying water vapour in the regenerator at 920°C. The temperature of the carbonator held stable around 630°C in all cases. The maximum carbonation conversion $X_{max,ave}$ observed for the cases when water vapour is involved is around double in comparison to previous experiments without water vapour. Increased carbonation conversion means increased carrying capacity of the sorbent, greater efficiency and less make-up flow Fo to compensate for the deactivated sorbent required. This way the overall feasibility of the process seems to be increased.

Moreover significant change of the surface of the sorbent is found. High surface is related with sorbent reactivity and is expected to decrease with time due to sintering processes. For the experimental cases with steam present, higher decrease rates of the surface area are reported. The increased $X_{max,ave}$ for this cases was attributed to a change in the sorbent pore structure, according to literature.

Regarding the carbonate content of the solids leaving the carbonator X_{carb} , very high values were achieved for the 1st experimental case and same to previous experiments without water vapour present for the 2nd and 3rd case. It was concluded that for the 1st case the reaction speed is increased. The increase in X_{carb} for the 1st set could be attributed to the possible improvement of heat transfer properties or sorbent properties due to water vapour.

As far as the carbonator efficiency E_{carb} is concerned, it is found to be an increasing function of looping ratio FCa/FCO₂. Moreover higher temperature gives higher E_{carb} values, since lower X_{calc} values are achieved. Water vapour in the carbonator results to increased carbonator efficiency for the same looping ratio values, due to the increased reaction speed. The effect of water vapour in the carbonator and the effect of higher temperature appears to be stronger than the space time, since it can be seen that the 2nd case with the highest space time presents the lowest efficiencies in comparison to those of the 1st and 3rd experimental case that have lower space time values. The 1st case with water vapour in both reactors presented great efficiency values are achieved for very low looping ratio values in comparison to

the other cases. In particular for a looping ration of only 3, an efficiency of around 80% was achieved. This is a very optimistic finding since low looping ratios are desirable. High looping ratios mean increased heat losses due to the increased circulation of solids.

Moreover the carbonator model proposed by Charitos et al [27] was used to validate the data occurred during the experiments. The fitting of experimental and model data provided the kinetic constant for the reaction, in particular $2s^{-1}$ for the 1^{st} set and 0.323 and 0.78s⁻¹ for the 2^{nd} and 3^{rd} set respectively. The higher ks value for the 1^{st} set with steam in both reactors is expected since higher reaction speed was observed for this case.

Regarding the carbonate content that remains in the solids leaving the regenerator X_{calc} , better values were observed for increasing water vapour partial pressure and similar regenerator residence time. Particular limitations exist due to the heat transfer capacity of the facility. For increasing residence time such limits are reached. Higher temperature results to higher calcination conversion limits.

As far as the efficiency of the regenerator E_{reg} is concerned in general increased values are observed for an increasing $t_{res,reg}/X_{carb}$ ratio for all of the experimental cases. Moreover the 1st and 3rd experimental cases present higher efficiencies than the 2nd case and the previous experimental data without water vapour involved. For the 1st case this is attributed to the water vapour presence in both reactors that resulted in higher X_{carb} values, whereas for the 3rd case to the increased temperature that resulted in lower X_{carb} values. For these two cases it can be observed that E_{Reg} values as high as 90% were achieved for only 50s of regenerator space time. For the same space time E_{Reg} values of only 60% are achieved for the 2nd case and for previous experiments without water vapour involved.

Furthermore, extended attrition was observed in the presence of water vapour, especially for the 1st case with water vapour present in both reactors. During this set blockages formed in the piping after the carbonator blocked the 1st cyclone impeding the recirculation of the sorbent. Regarding PSD the larger and therefore heavier particles that could not be lifted by the respective high velocities were found in the bed of the carbonator. The lowest median diameter dp₅₀ was found for particles of the 1st set with water vapour in both reactors. The lower particle size was probably attributed to increased attrition due to a softening effect of water vapour.

It is proposed that future experimental campaigns will further investigate the effect on the regeneration process of water vapour present only in the carbonator. Conclusively the results of this work are quite optimistic; water vapour appears to generally benefit the Calooping process. However further investigation on a larger scale would be useful for the scale-up process.

7 Bibliography

- "http://www.eea.europa.eu/data-and-maps/indicators/atmospheric-greenhouse-gasconcentrations-2/assessment-1#eea-comments," European Environmental Agency, January 2013. [Online].
- [2] IEA, "http://www.iea.org,"May2012.[Online].Available:http://www.iea.org/newsroomandevents/news/2012/may/globalcarbon-
dioxideemissionsincreaseby10gtin2011torecordhigh.html.Available:
- [3] IEA, "Energy technology perspectives 2012: Pathways to a clean energy system," OECD/IEA, France, 2012b.
- [4] E. Commission, "CO₂ Capture and Storage," *ec.europa.eu/energy/coal/ccs_en.htm*, 2009.
- [5] P. Konstantin, Praxisbuch Energiewirtschaft, Springer, 2009.
- [6] A. Charitos, C. Hawthorne, A. R. Bidwe, S. Sivalingam, A. Schuster, H. Spliethoff und G. Scheffknecht, "Parametric investigation of the calcium looping process for CO₂ capture in a 10kWth dual fluidized bed," *International Journal of Greenhouse Gas Control*, pp. 776-784, 23 May 2010.
- [7] A. Sanchez-Biezma, J. C. Ballesteros, E. d. Z. L. Diaz, F. J. Alvarez, J. Lopez, B. Arias, G. Grasa und J. C. Abanades, "Postcombustion CO2 capture with CaO. Status of the technology and next steps towards large scale demonstration," *Energy Procedia*, pp. 852-859, 2011.
- [8] A. Sieminski, "International Energy Outlook 2013," U.S. Energy Information Administration, Washington, DC, 2013.
- [9] I. Martinez, G. Grasa, R. Murillo, B. Arias und J. C. Abanades, "Modelling the continuous calcination of CaCO₃ in a Ca-looping system," *Chemical Engineering Journal*, pp. 174-181, 10 November 2012.
- [10] F. Gagelmann und B. Hansjürgens, "Climate Protection through Tradeable Permits: The EU Proposal for a CO₂ Trading System in Europe," *European Environment*, pp. 185-202, 2002.
- [11] M. d. Elzen, "Countries' mitigation commitments under the "South-North dialogue" proposal compatible with the EU 2°C target," Netherlands Environmental Assessment Agency.
- [12] W. Wang, S. Ramkumar und L.-S. Fan, "Energy Penalty of CO₂ Capture for the Carbonation-Calcination Reaction (CCR) Process: Parametric Effects and Comparisons

with Alternative Processes," Fuel, pp. 561-574, 21 May 2012.

- [13] J. Karg, "IGCC experience and further developments to meet CCS market needs," COAL-GEN, Katowice, Poland, 2009.
- [14] I. p. o. c. change, "Carbon Dioxide Capture and Storage," ipcc.ch, 2005.
- [15] J. Ströhle, A. Galloy und B. Epple, "Feasibility Study on the Carbonate Looping Process for Post-Combustion CO₂ Capture from Coal-Fired Power Plants," *Energy Procedia*, pp. 1313-1320, 2009.
- [16] N. Rodriguez, R. Murillo und a. J. C. Abanades, "CO₂ Capture from Cement Plants Using Oxyfired Precalcination and/or Calcium Looping," *Environmental Science & Technology*, pp. 2460-2466, 10 January 2012.
- [17] B. Arias, G. Grasa, J. C. Abanades, V. Manovic und E. J. Anthony, "The Effect of Steam on the Fast Carbonation Reaction Rates of CaO," *Industrial & Engineering Chemistry Research*, pp. 2478-2482, 5 January 2012.
- [18] L. M. Romeo, J. C. Abanades, J. M. Escosa, J. Pano, A. Gimenez, A. Sanchez-Biezma und J. C. Ballesteros, "Oxyfuel carbonation/calcination cycle for low cost CO₂ capture in existing power plants," *Elsevier*, pp. 2809-2814, 12 May 2008.
- [19] C. A. Hendriks, E. Worrell, D. d. Jager, K. Blok und P. Riemer, "Emission Reduction of Greenhouse Gases from the Cement Industry," *IEA Greenhouse Gas R& D Programme*, 23 August 2004.
- [20] E. Worrell, L. Price, N. Martin, C. Hendriks und L. O. Meida, "Carbon Dioxide Emissions from the Global Cement Industry," *Annual Review of Energy and the Environment*, pp. 303-329, 2001.
- [21] L. M. Romeo, D. Catalina, P. Lisbona, Y. Lara und A. Martinez, "Reduction of greenhouse gas emissions by integration of cement plants, power plants, and CO₂ capture systems," *Greenhouse Gases Science and Technology*, pp. 72-82, 2011.
- [22] P. Basu, Combustion and Gasification in Fluidized Beds, Taylor & Francis Group LLC, 2006.
- [23] O. Levenspiel, Chemical Reaction Engineering, John Wiley & Sons, Inc, 1999.
- [24] D. Kunii und O. Levenspiel, Fluidization Engineering, Butterworth Heinemann.
- [25] J. C. Dille, "Particle Ejection Mechanisms Due to Bubble Eruptions in Fluidized Beds," Lehigh University, 1981.
- [26] P. A. Berman und J. C. Dille, "HIGH EFFICIENCY PRESSURIZED FLUID BED SYSTEMS," THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS, pp. 345 E. 47 St., New York, NY 1001 7.

- [27] A. Charitos, N. Rodrigez, C. Hawthorne, M. Alonso, M. Zieba, B. Arias, G. Kopanakis, G. Scheffknecht und J. C. Abanades, "Experimental Validation of the Calcium Looping CO₂ Capture Process with Two Circulating Fluidized Bed Carbonator Reactors," *Industrial & Engineering Chemistry Research*, pp. 9685-9695, 20 June 2011.
- [28] A. Charitos, C.Hawthorne, A. R. Bidwe, L. Korovesis, A. Schuster und G. Scheffknecht, "Hydrodynamic Analysis of a 10kWth Calcium Looping Dual Fluidized Bed for postcombustion CO2 capture," *Powder Technology*, pp. 117-127, 19 February 2010.
- [29] Nuria Rodriguez et al, "Comparison of experimental results from three dual fluidized bed test facilities capturing CO₂ with CaO," *Energy Procedia*, pp. 393-401, 2011.
- [30] C. J. Abanades, E. J. Anthony, D. Alvarez et al "In-Situ Capture of CO₂ in a Fluidized Bed Combustor," In 17th International conference on Fluidized Bed Combustion, Florida, 2007.
- [31] S. Yang und Y. Xiao, "Steam Catalysis in CaO Carbonation under Low Steam Partial Pressure," *Industrial & Engineering Chemistry Research*, pp. 4043-4048, 16 May 2008.
- [32] V. Manovic und E. J. Anthony, "Carbonation of CaO-Based Sorbents Enhanced by Steam Addition," *Industrial & Engineering Chemistry Research*, pp. 9105-9110, 9 March 2010.
- [33] F. Donat, N. H. Florin, E. J. Anthony und P. S. Fennell, "Influence of High-Temperature Steam on the Reactivity of CaO Sorbent for CO₂ Capture," *Environmental Science & Technology*, pp. 1262-1269, 14 December 2011.
- [34] I. Linden, P. Backman, A. Brink und M. Hupa, "Influence of Water Vapor on Carbonation of CaO in the Temperature Range 400-550°C," *Industrial & Engineering Chemistry Research*, pp. 14115-14120, 28 Oktober 2011.
- [35] R. T. Symonds, D. Y. Lu, R. W. Hughes, E. J. Anthony und A. Macchi, "CO₂ Capture from Simulated Syngas via Cyclic Carbonation/Calcination for a Naturally Occuring Limestone: Pilot Plant Testing," *Industrial & Engineering Chemistry Research*, pp. 8431-8440, 4 August 2009.
- [36] P. Sun, J. R. Grace, C. J. Lim und E. J. Anthony, "Investigation of Attempts to Improve Cyclic CO₂ Capture by Sorbent Hydration and Modification," *Industrial & Engineering Chemistry Research*, pp. 2024-2032, 15 February 2008.
- [37] I. Martinez, G. Grasa, R. Murillo, B. Arias und J. C. Abanades, "Kinetics of Calcination of Partially Carbonated Particles in a Ca-Looping System for CO₂ Capture," *Energy & Fuels*, pp. 1432-1440, 2 January 2012.
- [38] T. Shimizu, T. Hirama, H. Hosoda, K. Kitano, M. Inagaki und K. Tejima, "A Twin Fluid-

Bed Reactor for Removal of CO_2 from Combustion Processes," *IChemE*, pp. 62-68, 1999.

- [39] J. Adanez, F. Garcia-Labiano et al "Calcination of calcium-based sorbents at pressure in a broad range of CO₂ concentrations," *Chemical Engineering Science Volume 57, Issue* 13, pp. 2381-2393, 2002.
- [40] Y. H. Khraisha und D. R. Dugwell, "Effect of water vapour on the calcination of limestone and raw meal in a suspension reactor," *IChemE*, pp. 76-78, January 1991.
- [41] R. S. Boynton, Chemistry and technology of lime and limestone, 2nd edition, New York: John Wiley, 1980.
- [42] W. H. MacIntire und T. B. Stansel, "Steam Catalysis in Calcinations of Dolomite and Limestone Fines," *Industrial and Engineering Chemistry*, pp. 1548-1555, 1953.
- [43] Y. Wang und W. J. Thomson, "The Effects of Steam and Carbon Dioxide on Calcite Decomposition Using Dynamic X-Ray Difractation," *Chemical Engineering Science*, pp. 1373-1382, 1995.
- [44] Y. Wang, S. Lin und Y. Suzuki, "Limestone Calcination with CO₂ Capture (II): Decomposition in CO₂/Steam and CO₂/N₂ Atmospheres," *Energy & Fuels*, pp. 2326-2331, 6 November 2008.
- [45] B. Gonzalez, G. S. Grasa und M. A. J. Abanades, "Modeling of the Deactivation of CaO in a Carbonate Loop at High Temperatures of Calcination," *Industrial & Engineering Chemistry Research*, pp. 9256-9262, 4 November 2008.
- [46] G. S. Grasa und J. C. Abanades, "CO₂ Capture Capacity of CaO in Long Series of Carbonation/Calcination Cycles," *INdustrial & Engineering Chemistry Research*, pp. 8846-8851, 2006.
- [47] G. D. Silcox, J. C. Kramlich und D. W. Pershing, "A Mathematical Model for the flash Calcination of Dispersed CaCO₃ and Ca(OH)₂ Particles," *Industrial & Engineering Chemistry Research*, pp. 155-160, 1989.
- [48] Z. Chen, J. R. Grace und C. J. Lim, "Limestone particle attrition and size distribution in a small circulating fluidized bed," *Fuel*, pp. 1360-1371, 18 July 2007.
- [49] P. Sun, J. R. Grace, C. J. Lim und E. Anthony, "The Effect of CaO Sintering on Cyclic CO₂ Capture in Energy Systems," *AIChE Journal*, pp. 2432-2442, 20 July 2007.
- [50] R. H. Borgwardt, "Calcium Oxide Sintering in Atmospheres Containing Water and Carbon Dioxide," *Industrial & Engineering Chemistry Research*, pp. 493-500, 1989.
- [51] S. Champagne, D. Y. Lu, A. Macchi, R. T. Symonds und E. J. Anthony, "Influence of Steam Injection during Calcination on the Reactivity of CaO-Based Sorbent for Carbon

Capture," *Industrial & Engineering Chemistry Research*, pp. 2241-2246, 28 December 2012.

- [52] F. Scala, A. Cammarota, R. Chirone und P. Salatino, "Comminution of Limestone During Batch Fluidized-Bed Calcination and Sulfation," *AIChE Journal*, pp. 363-373, February 1997.
- [53] J. Werther und J. Reppenhagen, Attrition in Fluidized Beds and Pneumatic Conveying Lines, 1998.
- [54] B. Gonzalez, M. Alonso und J. C. Abanades, "Sorbent attrition in a carbonation/calcination pilot plant for capturing CO₂ from flue gases," *Fuel*, pp. 2918-2924, 29 January 2010.
- [55] Politecnico di Milano, Alstom UK, "European best practice guidelines for assessment of CO₂ capture technologies," 2011.
- [56] D. Alvarez und J. C. Abanades, "Determination of the critical product layer thickness in the reaction of CaO with CO₂," *Industrial & Engineering Chemistry Research*, pp. 5608-5615, 16 June 2005.
- [57] E. Baker "The calcium oxide-carbon dioxide system in the pressure range of 1-300 atmospheres," *J Chem Soc,* pp. 464-470, 1962.
- [58] G. D. (Varela), I. Papandreou, A. Bidwe, V. Stack-Lara, H. Dieter und G.Scheffknecht, "Calcium looping process for CO₂ capture: Experimental characterization of the regenerator operation under oxy-fuel conditions, in a 10kWth dual fluidized bed facility (in press)". *Energy Procedia.*
- [59] S. Ramkumar und L.-S. Fan, "Thermodynamic and Experimental Analyses of the Three-Stage Calcium Looping Process," *Industrial & Engineering Chemistry Research*, pp. 7563-7573, 20 July 2010.
- [60] R. Barker, "The Reversibility of the Reaction CaCO₃-CaO+CO₂," Journal of Applied Chemistry and Biotechnology, pp. 733-742, 6 September 1973.
- [61] A. Bidwe, C. Hawthorne, A. Charitos et al "Cold model investigatoins of a high temperature looping process in a dual circulating fluidized bed," in *10th international conference on circulating fluidized beds combustion*, Oregon, USA, 2011.

8 Annex



Figure 8.1: a) 36ULS sample one, 2nd set with steam in Reg-900°C **b)** 37LLS sample one, 2nd set with steam in Reg-920°C



Figure 8.2: a) Crack that could lead to attrition by fragmentation b) Example of impurity of the sorbent



Figure 8.3: a) Candle filters - exit of carbonator b) 2nd cyclone - exit of carbonator



Figure 8.4: a) Sample 18LLS-1st set, steam in both carbonator and regenerator-900°C **b)** Sample 53LLS-3rd set, steam in the regenerator-920°C



Figure 8.5: a), b) Agglomeration in the 1st cyclone of the regenerator



Figure 8.6: Carbonator bed, 1st experimental set, steam in Carb and Reg



Figure 8.7: a)2nd cyclone of the carbonator

b)Calcined raw material



Figure 8.8: Matlab result for TGA calcination measurement



Figure 8.9: Matlab result for TGA carbonation measurement

Institute of Combustion and Power Plant Technology





ıfk

Director: Prof. Dr. techn. G. Scheffknecht Pfaffenwaldring 23 • 70569 Stuttgart Phone +49 (0) 711-685 63487 • Fax +49 (0) 711-685 63491

Experimental investigation of the effect of water vapour on the Ca-looping process at a 10kWth Dual Fluidized Bed facility

Πειραματική διερεύνηση της επίδρασης του ατμού στην διεργασία 'Calcium Looping' σε μία διπλή ρευστοποιημένη κλίνη των 10kW_{th}

<u>ΠΕΡΙΛΗΨΗ</u>

Σταυρουλάκης Εμμανουήλ Αρ. Μητρώου: 02108674

<u>Εισαγωγή</u>

Το διοξείδιο του άνθρακα (CO₂) είναι ο κύριος παράγοντας υπεύθυνος για την αύξηση της θερμοκρασίας του πλανήτη και φαινόμενα κλιματικής αλλαγής λόγω του φαινομένου του θερμοκηπίου. Παράγεται κυρίως από εργοστάσια παραγωγής ηλεκτρικής ενέργειας που χρησιμοποιούν κάρβουνο ως καύσιμο, ενώ παρουσιάζει μία διαρκώς αυξητική τάση. Η δέσμευση του CO₂ με βάση την διεργασία 'Calcium Looping' είναι μία υποσχόμενη τεχνολογία υπό ανάπτυξη, που βασίζεται στην αντίδραση μεταξύ CO₂ - οξειδίου του ασβεστίου (CaO) που σχηματίζει ανθρακικό ασβέστιο (CaCO₃), καθώς και στην αντίστροφη αντίδραση που παράγει ξανά CaO και ένα ρεύμα πλούσιο σε CO₂.

Η διπλωματική αυτή επικεντρώνεται στη μελέτη της επίδρασης του υδρατμού στη διεργασία αυτή, καθότι νερό (H₂O) εμπεριέχεται στο κάρβουνο και ως εκ τούτου απαντάται στα καυσαέρια της εκάστοτε μονάδας. Ακόμη νερό θα υπάρχει και στον αντιδραστήρα 'regenerator' όπου γίνεται απελευθέρωση του CO₂, εξαιτίας της καύσης παρουσία καθαρού οξυγόνου oxy-fired combustion' προκειμένου να επιτευχθεί η απαραίτητη υψηλή ενέργεια για την διεργασία της απελευθέρωσης του CO₂ (calcination).

Μία ρευστοποιημένη κλίνη ανακυκλοφορίας (Circulating Fluidized Bed) χρησιμοποιήθηκε ως αντιδραστήρας δέσμευσης του CO₂ (carbonator) στους 630 °C και μία αναβράζουσα ρευστοποιημένη κλίνη (Bubbling Fluidized Bed) ως 'regenerator' στους 900 με 920 °C. Τα αποτελέσματα έδειξαν αυξημένη ικανότητα δέσμευσης του CO₂ από το στερεό CaO. Ακόμη παρατηρήθηκε σημαντική βελτίωση της ικανότητας του 'carbonator' να δεσμεύει CO₂ για χαμηλότερους ρυθμούς κυκλοφορίας υλικού (looping ratio), σε σχέση με παλαιότερα πειράματα χωρίς παρουσία υδρατμού. Όσον αφορά την απόδοση του 'regenerator' παρατηρήθηκαν υψηλές τιμές μετατροπής του CaCO₃ πάνω από 80%. Τέλος όσον αφορά τις απώλειες υλικού 'attrition', υψηλές τιμές παρατηρήθηκαν σε σχέση με παλαιότερα πειράματα χωρίς υδρατμό.

Ενσωμάτωση της διεργασίας Ca-looping

Το ακόλουθο σχήμα παρουσιάζει τη διεργασία 'Calcium Looping' όπως αυτή θα ενσωματωθεί σε ένα εργοστάσιο παραγωγής ηλεκτρικής ενέργειας. Το καυσαέριο προερχόμενο από το εργοστάσιο εισέρχεται στον αντιδραστήρα 'carbonator' όπου λαμβάνει χώρα η δέσμευση του CO₂. Το φτωχό σε CO₂ ρεύμα καυσαερίων εξέρχεται στην ατμόσφαιρα, ενώ τα στερεά προχωρούν στον αντιδραστήρα 'regenerator'. Εκεί το CO₂ δεσμεύεται και ένα ρεύμα πλούσιο σε CO₂ οδηγείται για συμπίεση και αποθήκευση. Στο σχήμα διακρίνεται και η μονάδα ASU – air separation unit, η οποία παράγει το οξυγόνο που απαιτείται για τη καύση στον 'regenerator' για την επίτευξη των υψηλών θερμοκρασιών στον αντιδραστήρα αυτό.



Ακόμη στο ακόλουθο σχήμα παρατηρούμε τη δυνατότητα για εκμετάλλευση της σημαντικής ποσότητας θερμότητας που προκύπτει στα διάφορα μέρη της εγκατάστασης, μειώνοντας έτσι το κόστος της τεχνολογίας αυτής.



Με Q₁ συμβολίζεται η θερμότητα ανακτώμενη από τον 'carbonator' καθώς η αντίδραση δέσμευσης του CO₂ είναι εξώθερμη. Με Q₂ η θερμότητα ανακτώμενη από τα φτωχά σε CO₂ καυσαέρια που εξέρχονται από τον 'carbonator', ενώ με Q₃ η θερμότητα ανακτώμενη από το αντίστοιχο πλούσιο σε CO₂ ρεύμα καυσαερίων του 'regenerator'. Τέλος με Q₄ συμβολίζεται η θερμότητα ανακτώμενη από το θερμό ρεύμα στερεών που εξέρχεται από τον 'regenerator'. Το ρεύμα αυτό συνίσταται από την ανανέωση υλικού που έχει χάσει την ικανότητα του να αντιδρά, από τέφρα που προέκυψε κατά την καύση και από θειικό ασβέστιο CaSO₄ αν η μονάδα χρησιμοποιείται και ως εγκατάσταση αποθείωσης.

Τεχνολογία ρευστοποιημένων κλινών

Η τεχνολογία των ρευστοποιημένων κλινών είναι αρκετά διαδεδομένη και χρησιμοποιείται σε διάφορες εφαρμογές, στη χημική βιομηχανία και σε διεργασίες που περιλαμβάνουν καύση. Πρόκειται για αντιδραστήρες που βασίζονται στην μεταφορά θερμότητας και μάζας μέσω της διεπαφής στερεού – αερίου και παρουσιάζουν πλεονεκτήματα όπως καλύτερο συντελεστή επαφής κατά την αντίδραση και ομογένεια κατά τη μεταφορά θερμότητας.

Υπάρχουν διαφορετικοί τύποι ρευστοποιημένων κλινών ανάλογα με την ταχύτητα ρευστοποίησης. Η αναβράζουσα ρευστοποιημένη κλίνη (bubbling fluidized bed-BFB) χρησιμοποιεί χαμηλές ταχύτητες ρευστοποίησης. Μεγάλες φυσαλίδες σχηματίζονται μέσα στο στερεό με αποτέλεσμα χειρότερη επαφή που δυσχεραίνει την αντίδραση δέσμευσης του CO₂ από το CaO. Η ανακυκλοφορούσα ρευστοποιημένη κλίνη (circulating fluidized bed-CFB) από την άλλη πλευρά χρησιμοποιεί μεγαλύτερες ταχύτητες ρευστοποίησης, ενώ υπάρχει καλύτερος συντελεστής επαφής στερεού-αερίου. Τα στερεά εξέρχονται από την κορυφή του αντιδραστήρα αυτού και οδηγούνται πίσω στη βάση του μέσω αγωγού. Το ακόλουθο σχήμα επεξηγεί τους δύο τύπους ρευστοποιημένων κλινών:



Αντίδραση δέσμευσης-απελευθέρωσης CO₂ (carbonation-calcination)

Η διεργασία του 'calcium looping' στην οποία αναφέρεται η διπλωματική βασίζεται στην παρακάτω αντιστρεπτή αντίδραση, σύμφωνα με την οποία το CO₂ δεσμεύεται στον 'carbonator' και έπειτα απελευθερώνεται στον 'regenerator':

$$CaO + CO_2 \leftrightarrow CaCO_3$$
 $\Delta H = \pm 178 \text{ kJ/mol}$

Η αντίδραση καθορίζεται από τους παράγοντες θερμοκρασία και μερική πίεση CO₂ σύμφωνα με το παρακάτω διάγραμμα που προκύπτει με χρήση της εξίσωσης

logP(atm) = 7.079 -
$$\frac{8308}{T(K)}$$



Καθώς μελετάμε την επίδραση του υδρατμού πρέπει να εξετάσουμε την περίπτωση της αντίδρασης με το ασβέστιο Ca όπως φαίνεται από τα παρακάτω:

 $\begin{aligned} & \text{CaO} + \text{H}_2\text{O} \ \leftrightarrow \text{Ca(OH)}_2 \\ & \text{Ca(OH)}_2 + \text{CO}_2 \ \rightarrow \text{CaCO}_3 + \ \text{H}_2\text{O} \end{aligned}$

Όμως όπως φαίνεται από το παρακάτω διάγραμμα που προκύπτει από την εξίσωση

$$P_{H_20}(Pa) = 9 * 10^{11} * exp\left(\frac{-12531.5}{T(K)}\right)$$

στις συνθήκες του πειράματος δεν ήταν δυνατό να λάβει χώρα τέτοια αντίδραση.



Χημικές και μηχανικές ιδιότητες του ασβεστόλιθου

Η διπλωματική αυτή εξετάζει ακόμη τις χημικές και μηχανικές ιδιότητες του στερεού αντιδρώντος. Έτσι για τον ασβεστόλιθο έχει παρατηρηθεί ότι όσο υπόκειται σε διαδοχικές αντιδράσεις δέσμευσης-απελευθέρωσης, τείνει να χάνει την ικανότητά του να αντιδρά, στην αρχή γρήγορα και έπειτα πιο αργά καθώς φτάνει σε μία παραμένουσα ελάχιστη ικανότητα αντίδρασης. Η ακόλουθη εξίσωση και το αντίστοιχο διάγραμμα έχουν προταθεί για την περιγραφή της ικανότητας του ασβεστόλιθου να αντιδρά.

$$X_{N} = \frac{1}{\frac{1}{1 - X_{r}} + kN} + X_{r}$$



Τέλος μία άλλη πολύ σημαντική ιδιότητα είναι το 'surface area' σε m²/g, η επιφάνεια η οποία διατίθεται προς αντίδραση. Μεγάλη τιμή αυτού του μεγέθους σημαίνει μεγαλύτερη ικανότητα του στερεού να αντιδράσει. Η τιμή αυτή μειώνεται με την πάροδο του χρόνου στον αντιδραστήρα στην αρχή ραγδαία και έπειτα πιο αργά.

Όσον αφορά τις μηχανικές ιδιότητες του ασβεστόλιθου εξετάζεται η μείωση της διαμέτρου των κόκκων και συνεπώς ο ρυθμός απώλειας υλικού από τη μονάδα 'attrition'. Το μέγεθος αυτό είναι πολύ σημαντικό καθώς καθορίζει το ρυθμό με τον οποίο πρέπει να αναπληρώνουμε με φρέσκο υλικό και συνεπώς την οικονομική βιωσιμότητα της τεχνολογίας αυτής. Το 'attrition' παρουσιάζει μία αρχική υψηλή τιμή καθώς τα μαλακά σωματίδια οδηγούνται σε θραύση, η οποία ακολουθείται από πιο χαμηλές τιμές καθώς τα σωματίδια που έχουν μείνει στον αντιδραστήρα είναι τα πιο ανθεκτικά σε τυχόν συγκρούσεις και επιφανειακή φθορά. Πολλοί παράγοντες επηρεάζουν το φαινόμενο αυτό, αλλά από τους πιο σημαντικούς είναι η ταχύτητα ρευστοποίησης. Υψηλή ταχύτητα οδηγεί τα σωματίδια σε συγκρούσεις μεταξύ τους και με τα τοιχώματα και τα οδηγεί σε θραύση είτε σταδιακή μείωση της διαμέτρου. Το ακόλουθο σχήμα επεξηγεί τη διαδικασία του 'attrition'.



Στη διπλωματική αυτή εξετάζεται το φαινόμενο 'attrition' και η εξέλιξή του για διαφορετικές συνθήκες ύπαρξης υδρατμών, προκειμένου να καθοριστεί η επίδραση της συγκέντρωσης H₂O στο φαινόμενο αυτό.

<u>Στόχος εργασίας</u>

Η διπλωματική αυτή φιλοδοξεί να συμβάλλει στην γνώση της επίδρασης του ατμού στην διεργασία 'Ca-looping', αντικείμενο το οποίο δεν έχει διερευνηθεί επαρκώς έως τώρα, ενώ τα αποτελέσματα που προκύπτουν από τη βιβλιογραφία είναι συχνά αντικρουόμενα. Ακόμη στην πλειοψηφία της η σχετική έρευνα έχει διεξαχθεί σε μικρές μονάδες TGA 'thermogravimetric analysers' και σε πολύ μικρό βαθμό σε μονάδες της κλίμακας των 10 kW_{th}, όπως στη δική μας περίπτωση. Ο ατμός παίζει πολύ σημαντικό ρόλο καθώς τα περισσότερα ορυκτά καύσιμα περιέχουν σημαντική ποσότητα υγρασίας, η οποία εντοπίζεται στα καυσαέρια υπό μορφή υδρατμού σε συγκεντρώσεις 5-10%, τιμή η οποία ποικίλλει ανάλογα τον τύπο του καυσίμου.

Η μελέτη της επίδρασης του ατμού θα πρέπει να γίνει σε σχέση με την απόδοση του 'carbonator', του 'regenerator' και συνολικά την απόδοση της μονάδας και σε σχέση με τη μέγιστη ικανότητα μετατροπής Xmax του στερεού αντιδρώντος καθώς και το ρυθμό αντίδρασης του. Επιπλέον αναγκαία είναι η μελέτη της επίδρασης στις μηχανικές και χημικές ιδιότητες του αντιδρώντος στερεού, καθώς και ο ρυθμός απώλειας υλικού 'attrition' προκειμένου να γνωρίζουμε την απαραίτητη ροή φρέσκου υλικού 'make-up flow'.

Τέλος η διπλωματική αυτή φιλοδοξεί να συμβάλλει στο 'scaling up' της τεχνολογίας αυτής. Καθώς αποτελεί το βήμα μεταξύ πολύ μικρών πειραματικών μονάδων και βιομηχανικής κλίμακας της τάξης των 200 kW_{th} και 1 MW_{th}.

Πειραματικό πρόγραμμα και εγκατάσταση

Στα πλαίσια της διπλωματικής αυτής εργασίας πραγματοποιήθηκαν τρεις ομάδες πειραμάτων. Μελετήθηκε η επίδραση του ατμού στις περιπτώσεις όπου αυτός ήταν παρών και στους δύο αντιδραστήρες ή και μόνο στον 'regenerator'. Αναλυτικά τα πειραματικά 'σημεία' διακρίνονται στον παρακάτω πίνακα:

	Regenerator		Carbonator			
Steady State	T (°C)	CO2inDRY (%)	H2Oin (%)	T (°C)	CO2inDRY (%)	H2Oin (%)
1	900	60	15	630	14	8
2	900	60	20	630	14	8
3	900	60	20	630	14	8
4	900	60	30	630	14	8
5	900	60	30	630	14	8
6	900	60	25	630	14	8
7	900	60	25	630	14	8
8	900	60	35	630	14	8
9	900	60	0	630	14	-
10	900	60	10	630	14	-
11	900	60	20	630	14	-
12	900	60	30	630	14	-
13	900	60	40	630	14	-
14	920	60	0	630	14	-
15	920	60	10	630	14	-
16	920	60	20	630	14	-
17	920	60	20	630	14	-
18	920	60	30	630	14	-
19	920	60	0	630	14	-
20	920	60	40	630	14	-

Συγκεκριμένα στην πρώτη ομάδα πειραματικών σημείων μελετήθηκε η επίδραση του ατμού και στους δύο αντιδραστήρες, στη δεύτερη ομάδα η επίδραση μόνο στον 'regenerator', ενώ στην τρίτη η επίδραση στον 'regenerator' σε συνδυασμό όμως με υψηλότερη θερμοκρασία αντίδρασης – 920°C αντί 900°C όπως στην πρώτη και δεύτερη ομάδα. Τέλος τα παραπάνω πειραματικά αποτελέσματα συγκρίθηκαν με προηγούμενα πειράματα στη μονάδα χωρίς παρουσία ατμού.

Για μία τυπική σύσταση άνθρακα έγιναν υπολογισμοί για στοιχειομετρική καύση. Παρουσιάζεται στον ακόλουθο πίνακα η αντίστοιχη τυπική σύσταση καυσαερίου και οι συγκεντρώσεις υδρατμού για καύση με ξηρό ή ατμοσφαιρικό αέρα.

Flue gas composition (Typical Hardcoal)							
CO ₂	SO ₂	N ₂	H ₂ O _{d.a.}	H ₂ O _{ha}			
17.31%	0.05%	75.29%	7.31%	8.25%			

Για την περίπτωση της καύσης με καθαρό οξυγόνο (oxy-fired combustion) οι υπολογισμοί δίνουν συγκέντρωση υδρατμών 30% αν δε ληφθεί υπόψη η ανακυκλοφορία καυσαερίου και το CO₂ που απελευθερώνεται από τον ασβεστόλιθο.

Περιγραφή εγκατάστασης



Η πειραματική εγκατάσταση απεικονίζεται σχηματικά παρακάτω:

Διακρίνονται ο αντιδραστήρες 'regenerator' και 'carbonator' όπου γίνεται η απελευθέρωση και δέσμευση του CO₂ αντίστοιχα. Ακόμη διακρίνονται οι 'μικρές' ρευστοποιημένες κλίνες 'upper loop seal' και 'lower loop seal' οι οποίες εξασφαλίζουν ότι δεν έχουμε μετακίνηση αερίου από τον ένα αντιδραστήρα στον άλλο, καθώς και η κωνική βαλβίδα η οποία ρυθμίζει το ρυθμό ροής στερεού υλικού μεταξύ των δύο αντιδραστήρων και αποτελεί καινοτομία της μονάδας αυτής. Προθερμαντήρες χρησιμοποιούνται για να επιτευχθεί κατάλληλη θερμοκρασία εισόδου των αερίων στις κλίνες, ενώ τα καυσαέρια εξέρχονται μέσω κυκλώνων οι οποίοι κατακρατούν τα στερεά σωματίδια. Τέλος υπάρχουν αναλυτές της σύστασης των καυσαερίων στην έξοδο κάθε αντιδραστήρα.

<u>Αποτελέσματα και συμπεράσματα</u>

Εγκυρότητα αποτελεσμάτων

Το παρακάτω διάγραμμα πιστοποιεί την εγκυρότητα των πειραματικών σημείων. Υποδεικνύει ότι για τις συγκεκριμένες συνθήκες διεξαγωγής του πειράματος είχαμε είτε δέσμευση είτε απελευθέρωση CO₂ αντίστοιχα όπως περιμέναμε.



Thermodynamic Equilibrium Curve

Figure: Experimental Points - Steady States on the Thermodynamic Equilibrium Curve Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

Ακόμη η μάζα του CO₂ που δεσμεύτηκε θα πρέπει να φαίνεται στα στερεά. Για επαλήθευση της παραπάνω βασικής αρχής έγινε χρήση της εξίσωσης:

$F_{CO_2} * E_{carb} = F_{Ca} * (X_{carb} - X_{calc})$

Τα παρακάτω δύο διαγράμματα υλοποιούν την βασική αυτή αρχή του ισοζυγίου μάζας για κάθε αντιδραστήρα ξεχωριστά. Παρατηρείται καλή συμφωνία των πειραματικών δεδομένων για τις περισσότερες των περιπτώσεων. Σημεία που απέχουν από το αναμενόμενο μπορεί να αποδοθούν σε ανακρίβεια των μετρητικών διατάξεων, καθώς και στο σφάλμα που ενυπάρχει σε μονάδες τέτοιας κλίμακας.



Figure: Carbonator Mass Balance

Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C **Reg:** wet flue gas, 46% CO₂, rest N₂, 900°C **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C **Exp. case 3: Carb:** 14% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 61% CO₂, rest N₂, 920°C



Figure: Regenerator Mass Balance **Exp. case 1: Carb:** 16% CO₂, 8% H₂O, rest N₂, 630°C **Reg:** wet flue gas, 46% CO₂, rest N₂, 900°C **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C **Exp. case 3: Carb:** 14% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 61% CO₂, rest N₂, 920°C

Τέλος στα δύο επόμενα διαγράμματα παρουσιάζονται δύο χαρακτηριστικά 'steady state', ένα από κάθε αντιδραστήρα. 'Steady state' χαρακτηρίζεται ένα χρονικό διάστημα –για τις ανάγκες των συγκεκριμένων πειραμάτων περίπου 15min κατά το οποία βασικά μεγέθη παραμένουν σταθερά. Αυτά τα μεγέθη στην περίπτωση μας είναι θερμοκρασία και συγκεντρώσεις CO₂ στην είσοδο και έξοδο κάθε αντιδραστήρα. Έτσι μπορούμε να βεβαιώσουμε για κάθε πειραματικό σημείο ότι η τυχόν αλλαγή στο βαθμό απόδοσης οφείλεται στο μέγεθος υπό εξέταση – υδρατμό για την περίπτωσή μας.



Ερμηνεία πειραματικών αποτελεσμάτων

Μέγιστη ικανότητα πρόσληψης CO₂ - X_{max}

Στο πρώτο διάγραμμα φαίνεται η τιμή X_{max}, δηλαδή η μέγιστη ικανότητα του υλικού για αντίδραση – πρόσληψη CO₂. Στον άξονα χ παρατηρείται η συγκέντρωση του H₂O. Παρατηρούμε λοιπόν ότι διαφορετική συγκέντρωση δεν επηρεάζει την ικανότητα αντίδρασης, παρόλο που η ύπαρξη υδρατμού βελτιώνει την τιμή X_{max}. Σε γενικές γραμμές παρατηρείται η τάση μείωσης της X_{max} με την πάροδο του χρόνου παραμονής στον αντιδραστήρα.



Figure: The effect of water vapour partial pressure on $X_{max,ave}$ Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

Στο ακόλουθο διάγραμμα φαίνεται πάλι η τάση μείωσης με το χρόνο παραμονής στη μονάδα. Χρησιμοποιούνται οι θεωρητικοί κύκλοι αντίδρασης που είναι μέγεθος το οποίο βοηθάει στην κανονικοποίηση διαφορετικών μεταξύ τους συνθηκών και στη σύγκριση με παλαιότερα αποτελέσματα. Στο διάγραμμα φαίνεται ακόμα ότι η παραμένουσα ικανότητα αντίδρασης για όλες τις περιπτώσεις παρουσία ατμού είναι σχεδόν διπλάσια, αποτέλεσμα αρκετά ενθαρρυντικό ως προς τη συμβολή του υδρατμού στην βελτίωση της συνολικής απόδοσης της διεργασίας.



Figure: Maximum Carbonation Conversion versus Theoretical Cycles **Exp. case 1: Carb:** 16% CO₂, 8% H₂O, rest N₂, 630°C **Reg:** wet flue gas, 46% CO₂, rest N₂, 900°C **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C **Exp. case 3: Carb:** 14% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 61% CO₂, rest N₂, 920°C **Prev. experiments: Carb:** 12% CO₂, rest N₂,630°C **Reg:** dry flue gas, 53% CO₂, rest N₂, 900°C [58]

Επιφάνεια αντίδρασης – Surface area

Το μέγεθος 'surface area' συνδέεται με τη διαθέσιμη επιφάνεια στερεού προς αντίδραση και συνεπώς την ικανότητα του στερεού για δέσμευση CO₂. Το παρακάτω διάγραμμα παρουσιάζει την εξέλιξη αυτού του μεγέθους για κάθε μία πειραματική ομάδα. Η αρχική τιμή του μεγέθους είναι **7.98m²/g** για φρέσκο υλικό της πρώτης ομάδας πειραματικών σημείων και **6.22m²/g** για τη δεύτερη. Μετά από 6 ώρες και 30 λεπτά η τιμή έχει μειωθεί σε **1.73m²/g** για την πρώτη και έπειτα από περίπου 4 ώρες σε **3.01m²/g** για τη δεύτερη αντίστοιχα.

The lower value for the 1st set is expected since the material has undergone cyclic carbonation/calcination for more time, thus presenting increased sintering and less surface area. For the 3rd experimental set half older material was used that had already undergone sintering and half fresh calcined material was added.



Figure: Surface Area

Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C
Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C
Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

Ακόμη σύμφωνα και με το δεύτερο διάγραμμα παρατηρείται αυξημένη μείωση της τιμής 'surface area', που συμβαδίζει με τη βιβλιογραφία η οποία υποδεικνύει χειροτέρευση του μεγέθους αυτού για υψηλή θερμοκρασία και παρουσία υδρατμού. Παρόλα αυτά παρατηρήθηκε αυξημένη ικανότητα αντίδρασης παρουσία υδρατμού. Αυτό δικαιολογείται στη βιβλιογραφία με αλλαγή στη δομή και το πορώδες του υλικού, έτσι ώστε παρά τη μείωση του 'surface area' μετακίνηση προς μεγαλύτερους πόρους οδηγεί σε μείωση των φραγμένων πόρων και αυξημένη ικανότητα μετατροπής του CaO σε CaCO₃.


Figure: Surface Area Decrease Rate Sfinal/Soriginal

Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C **Reg:** wet flue gas, 46% CO₂, rest N₂, 900°C **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C **Exp. case 3: Carb:** 14% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 61% CO₂, rest N₂, 920°C **Prev. experiments: Carb:** 12% CO₂, rest N₂,630°C **Reg:** dry flue gas, 53% CO₂, rest N₂, 900°C [58]

Περιεχόμενο CO2 στα στερεά που εξέρχονται από τον 'carbonator' – Xcarb



Figure: Xcarb versus residence time of the carbonator **Exp. case 1: Carb:** 16% CO₂, 8% H₂O, rest N₂, 630°C **Reg:** wet flue gas, 46% CO₂, rest N₂, 900°C **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C **Exp. case 3: Carb:** 14% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 61% CO₂, rest N₂, 920°C Αυξημένη τιμή X_{carb} σημαίνει ότι ο αντιδραστήρας λειτούργησε καλά δεσμεύοντας αυξημένη ποσότητα CO₂. Αυτό παρατηρείται για την πρώτη πειραματική ομάδα παρουσία υδρατμού και στους δύο αντιδραστήρες.

<u>Βαθμός απόδοσης 'carbonator' (Ecarb)</u>

Το ακόλουθο διάγραμμα προκύπτει όσον αφορά το βαθμό απόδοσης του 'carbonator'. Ο βαθμός απόδοσης εκφράζεται συναρτήσει του 'looping ratio', ένα μέγεθος που δηλώνει την ποσότητα του στερεού υλικού που διατίθεται κάθε φορά για αντίδραση – δέσμευση CO₂. Παρατηρείται ότι υψηλή τιμή του μεγέθους αυτού συνδυάζεται με αυξημένη απόδοση. Παρόλα αυτά υψηλή τιμή αυτού του μεγέθους σημαίνει και αυξημένο κόστος λειτουργίας λόγω διακίνησης μεγαλύτερης μάζας στερεού αντιδρώντος. Όσον αφορά την επίδραση του ατμού παρατηρείται ραγδαία βελτίωση της απόδοσης παρουσία υδρατμού και στους δύο αντιδραστήρες. Πρόκειται για αρκετά ενθαρρυντικό εύρημα όσον αφορά την οικονομική βιωσιμότητα και αποδοτικότητα της διεργασίας αυτής.



Figure: Carbonator efficiency versus looping ratio and space time Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

<u>Περιεχόμενο CO₂ στα στερεά που εξέρχονται από τον 'carbonator' – X_{calc}</u>

Σημαντικό μέγεθος είναι επίσης η τιμή Xcalc, δηλαδή το περιεχόμενο CO₂ στα στερεά που εξέρχονται από τον 'regenerator'. Εδώ είναι επιθυμητή πολύ μικρή τιμή του μεγέθους αυτού, καθώς αυτό σημαίνει καλή λειτουργία του 'regenerator', δηλαδή μέγιστη απελευθέρωση του περιεχόμενου CO₂. Παρατηρείται στο ακόλουθο διάγραμμα βελτίωση της τιμής αυτής με αύξηση της περιεκτικότητας σε υδρατμό, μέχρι ορισμένα όρια μετατροπής του CaCO₃ σε CaO. Μέγιστη μετατροπή παρατηρείται για την τρίτη ομάδα πειραματικών δεδομένων με υψηλότερη θερμοκρασία αντίδρασης, γεγονός που επιβεβαιώνει τον κυρίαρχο ρόλο της θερμοκρασίας στην εξέλιξη της αντίδρασης.



Figure: Conversion of CaCO₃ to CaO versus water vapour partial pressure Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C

<u>Βαθμός απόδοσης του 'regenerator' (Ereg</u>)

Ο βαθμός απόδοσης του 'regenerator' δίνεται από την εξίσωση:

 $Ereg = \frac{Xcarb - Xcalc}{Xcarb}$



Figure: Regenerator efficiency versus regenerator load Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C Prev. experiments: Carb: 12% CO₂, rest N₂,630°C Reg: dry flue gas, 53% CO₂, rest N₂, 900°C [58]

Τα αποτελέσματα του παραπάνω διαγράμματος αποδίδονται για την μεν πρώτη ομάδα πειραματικών σημείων στην πολύ καλή τιμή του Xcarb που επιτεύχθηκε, για τη δε τρίτη ομάδα στην πολύ καλή – χαμηλή τιμή Xcalc, λόγω της υψηλότερης θερμοκρασίας.

Απώλεια υλικού – attrition

Η σημασία του ρυθμού με τον οποίο έχουμε απώλεια υλικού εξηγήθηκε και παραπάνω. Επηρεάζει άμεσα την αποτελεσματικότητα και οικονομική βιωσιμότητα της διεργασίας αυτής. Το ακόλουθο διάγραμμα παρουσιάζει το μέγεθος αυτό σε κιλά ανά ώρα λειτουργίας. Παρατηρείται ιδιαίτερα αυξημένο 'attrition' παρουσία υδρατμού, ειδικά για την περίπτωση όπου υδρατμός ήταν παρών και στους δύο αντιδραστήρες. Για την περίπτωση αυτή στη μονάδα παρατηρήθηκε επικάθιση στερεού υλικού στα τοιχώματα των σωληνώσεων και των κυκλώνων, δημιουργώντας προβλήματα στην ομαλή ροή – λειτουργία της μονάδας.



Figure: Mass loss per hour for different experimental conditions Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C Reg: wet flue gas, 46% CO₂, rest N₂, 900°C Exp. case 2: Carb: 10% CO₂, rest N₂, 630°C Reg: wet flue gas, 55% CO₂, rest N₂, 900°C Exp. case 3: Carb: 14% CO₂, rest N₂, 630°C Reg: wet flue gas, 61% CO₂, rest N₂, 920°C Prev. experiments: Carb: 12% CO₂, rest N₂,630°C Reg: dry flue gas, 53% CO₂, rest N₂, 900°C [58]

<u>Κοκκομετρία</u>

Το ακόλουθο διάγραμμα επιβεβαιώνει ότι το μέγεθος των κόκκων συνδέεται άμεσα με το φαινόμενο 'attrition'. Τα λεπτόκκοκα σωματίδια σταδιακά παρασέρνονται εκτός του συστήματος διαμέσου των κυκλώνων λόγω των υψηλών ταχυτήτων ρευστοποίησης. Έτσι παρατηρείται στην κλίνη να παραμένουν τα πιο χοντρόκκοκα – βαριά σωματίδια.



Figure: Particle size for raw calcined material, carbonator and regenerator bed **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C

Η σταδιακή φθορά – τριβή των σωματιδίων μεταξύ τους και με τα τοιχώματα των αντιδραστήρων οδηγεί στη σταδιακή μείωση των διαστάσεων τους και την πιθανή απώλειά τους διαμέσου των κυκλώνων. Η σταδιακή αυτή μείωση της διάμεσης διαμέτρου με την πάροδο του πειραματικού χρόνου φαίνεται και στο ακόλουθο διάγραμμα:



Figure: Median value of particle size – dp₅₀

Exp. case 1: Carb: 16% CO₂, 8% H₂O, rest N₂, 630°C **Reg:** wet flue gas, 46% CO₂, rest N₂, 900°C **Exp. case 2: Carb:** 10% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 55% CO₂, rest N₂, 900°C **Exp. case 3: Carb:** 14% CO₂, rest N₂, 630°C **Reg:** wet flue gas, 61% CO₂, rest N₂, 920°C **Prev. experiments: Carb:** 12% CO₂, rest N₂,630°C **Reg:** dry flue gas, 53% CO₂, rest N₂, 900°C [58]

<u>Επίλογος</u>

Τα ευρήματα αυτής της διπλωματικής εργασίας είναι ιδιαίτερης σημασίας για την υλοποίηση της διεργασίες του 'calcium looping' σε μεγαλύτερη κλίμακα και υπό ρεαλιστικές συνθήκες ύπαρξης σημαντικής ποσότητας υδρατμών στα καυσαέρια. Έδειξαν ωφέλιμη επίδραση του υδρατμού στην απόδοση της μονάδας όσον αφορά την ικανότητα δέσμευσης και απελευθέρωσης CO₂, καθώς και όσον αφορά την ικανότητα αντίδρασης του ασβεστόλιθου έπειτα από πολλούς κύκλους λειτουργίας. Από την άλλη πλευρά έδειξαν εκτεταμένες απώλειες υλικού και συνεπώς ανάγκη διαρκούς τροφοδοσίας με φρέσκο ασβεστόλιθο. Εν κατακλείδι η τεχνολογία αυτή προσφέρεται για τον περιορισμό του παραγόμενου CO₂ από μεγάλες μονάδες παραγωγής ενέργειας. Περαιτέρω μελέτη και οικονομοτεχνική βελτιστοποίηση είναι απαραίτητες για την αποτελεσματική ενσωμάτωση της τεχνολογίας αυτής στις εν λόγω μονάδες.