

Waste Ca (Eggshells) natural materials for CO₂ capture

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Abstract

The CO₂ produced by fossil fuels combustion is responsible by greenhouse gas effect and consequent global warming. Current international directives are aiming a drastic reduction of CO₂ emissions, which achieved by uses of renewable energy and CCS technologies implementation.

The Ca looping is proposed as a feasible technology for post combustion systems. The CaO is cyclic carbonated/decarbonated. However, lime sorbents suffer fast decay of CO₂ sorption capacity due to sinterization. In fact, the cyclic carbonation/decarbonation occurs at temperatures higher than the CaCO₃ Tammann temperature thus promoting sinterization.

In order to prepare lime sorbents in a sustainable manner with improved anti-sintering resistance eggshells were used as raw material. The as received eggshells were washed, grounded and calcined. The sorbents were modified with small amounts (5% w/w) of alkaline and alkaline earths carbonates, SiO₂ and ZrO₂. Dry-mixing and sol-gel like, using lactic acid as chelating agent, procedures were used to prepare modified sorbents.

The cyclic carbonation, performed by thermogravimetry using gas mixtures containing 20% (V/V) of CO₂ in N₂, showed that small amounts of dopant elements are able to improve the lime stability, probably by a monophasic spacer effect. As expected the sol-like process produced more stable sorbents.

Keywords: CO₂ capture, post- combustion, CCS, calcium cycle, sinterization, sol-gel

Resumo

O CO₂, resultante da queima de combustíveis de origem fóssil, é considerado o poluente responsável pelo efeito de estufa e conseqüente aquecimento global. Atualmente existem directivas, a nível mundial, para a redução drásticas das emissões de carbono o que pode ser conseguido com recurso combustíveis renováveis e a tecnologias de captura e armazenamento de carbono.

O ciclo do cálcio adequado para a captura de CO₂ a altas temperaturas, ou seja em sistemas de pós-combustão. No ciclo do cálcio, o CaO é carbonatado, para fazer a captura do CO₂, e posteriormente descarbonatado para recuperar o CaO. A sinterização, e conseqüente redução da capacidade de captura, é apontada como a maior desvantagem desta tecnologia.

Com o objectivo de preparar CaO com maior resistência à sinterização em processos de CCS, preparam-se amostras usando cascas de ovo. Procedeu-se à lavagem, moagem e calcinação das cascas de ovo para ser obter um pó fino, branco, que era essencialmente CaO. Adicionalmente foram preparadas amostras modificadas com carbonatos de metais alcalinos e alcalino terrosos e SiO₂ e ZrO₂ (5% mássico) recorrendo a processos de mistura a seco e processos do tipo sol-gel usando como agente quelante o ácido láctico.

A carbonatação/descarbonatação cíclica, avaliada por termogravimetria com misturas 20% CO₂/N₂, mostrou que pequenas quantidades de elementos dopantes tem um efeito apreciável na melhoria da resistência à sinterização do CaO actuando eventualmente como espaçador monofásico. O processo sol-gel conduziu como esperado a sorventes com maior capacidade inicial de captura de CO₂ e maior estabilidade.

Palavras chave: Captura de CO₂, pós combustão, CCS, ciclo do cálcio, sinterização, sol-gel

Index

Abstract.....	3
List of Figures	6
List of tables.....	8
1. Introduction.....	9
Objective of the thesis.....	10
Thesis outline.....	11
2. Literature review.....	12
CCS.....	12
CO ₂ transportation	18
CO ₂ storage	18
Economics of CO ₂ capture.....	19
Review of adsorbents used in CO ₂ capture [19].....	20
Calcium oxide - carbonate cycle	26
Recent improvements of a process/current development of improvements	32
Feedstock for Calcium Looping Cycle sorbent preparation	36
3. Materials and methods	39
Raw materials	39
Sorbent preparation	39
Techniques of sorbent characterization.....	41
4. Results and discussion.....	43
Specific surface area and pores characteristics	43
XRD Diffractograms of examined samples.....	44
Morphology of examined samples	46
Dynamic investigation by TGA.....	50
CO ₂ adsorption test in multicycle experiments.	54
Influence on performance of modifications applied	55
Effect of carbonate salts modification on sorbent performance.....	55
Performance of sorbents prepared by modification with lactic acid.....	60
Influence of decarbonation time on sorbent regenerability	62
Influence of sorption preparation method on performance.....	65

Longrun experiment performed for 25 cycles	67
5. Conclusions	69
References	70

List of Figures

Figure 1 projection of temperature rise, according to National Oceanic & Atmospheric Administration[94]	9
Figure 2 CO ₂ concentration levels and temperature evolution observed at Mauna Loa NOAA observation point [93].....	10
Figure 3 Electricity generation by source, according to International Energy Agency[5]	12
Figure 4 Available CCS technologies [95].....	13
Figure 5 Absorption apparatus and process schematics [96]	14
Figure 6 Membrane separation scheme [10].....	16
Figure 7 Proposed model of microalgae usage for CO ₂ capture[97]	17
Figure 8 Adsorption with PSA.....	18
Figure 9 Zeolite schematic structure	21
Figure 10 MOF-5 structure [33]	22
Figure 11 Molecular basket concept, dots are representing capture sites [36].....	23
Figure 12 Nitrogen surface active groups on activated carbon [39].....	24
Figure 13 Scheme of carbonation – calcination process in Calcium Looping Cycle application[98]	26
Figure 14 Calcination and carbonation presented in cycles [98].....	27
Figure 15 Schematics of Precombustion Calcium looping cycle application for biomass gasification [52]	28
Figure 16 Sintering of particles [99].....	30
Figure 17 Pore skeleton model [98]	33
Figure 18 CaO doped on zirconia approach [83]	36
Figure 19 Comparison between various type of bioderived CaO sorbents.....	37
Figure 20 XRD diffractograms of samples prepared with ZrO ₂ and SiO ₂	44
Figure 21 XRD diffractograms of sorbent prepared with carbonate salts	45
Figure 22 SEM images of calcined eggshells	46
Figure 23 SEM images of fresh Na ₂ CO ₃ modified samples	46
Figure 24 SEM images of fresh K ₂ CO ₃ modified samples.....	47
Figure 25 SEM images of fresh MgCO ₃ modified samples	47
Figure 26 SEM images of fresh MnCO ₃ modified sorbents.....	48
Figure 27 SEM images of fresh Li ₂ CO ₃ modified sorbent	48
Figure 28 SEM images of fresh SrCO ₃ modified sorbent.....	49
Figure 29 SEM images of fresh SiO ₂ dry mixed modified sorbent	49

Figure 30 SEM image of fresh SiO ₂ modified sorbent prepared by sol-gel like method (upper part) and fresh ZrO ₂ modified sorbent prepared by sol-gel like method (lower part).....	50
Figure 31 Thermograms of ZrO ₂ and SiO ₂ modified sorbents during dynamic test.....	51
Figure 32 Thermograms of sorbents modified with carbonate salts during dynamic tests	52
Figure 33 Sorption capacity with respect to mg CaO for sorbents prepared with ZrO ₂	53
Figure 34 DTG graphs for dynamic tests	54
Figure 35 Graphical representation of conditions during longruns.....	55
Figure 36 Thermograms for carbonate modified sorbents during longruns	56
Figure 37 Capture rate profiles during first (left) and last (right) cycle for carbonate modified sorbents longruns	57
Figure 38 SEM image of unmodified eggshells after 12th cycles of longrun tests.....	58
Figure 39 SEM images of Li ₂ CO ₃ (left) and SrCO ₃ (right) modified sorbents after longrun	59
Figure 40 SEM images of K ₂ CO ₃ (left top), MgCO ₃ (right top), Na ₂ CO ₃ (left bottom) and MnCO ₃ (right bottom) modified sorbents after longrun.....	60
Figure 41 Thermograms for sorbents prepared by sol-gel like method after longruns	61
Figure 42 Capture rate profiles for first (left) and last cycle during longruns of sol-gel like prepared sorbents	61
Figure 43 SEM images of ZrO ₂ (left) and SiO ₂ (right) modified sorbents prepared by sol-gel like method	62
Figure 44 Evolution of sorption capacity for ZrO ₂ modified sorbents vs. number of a cycle.....	63
Figure 45 Evolution of sorption capacity for SrCO ₃ modified sorbents vs. number of a cycle	63
Figure 46 SEM images of SrCO ₃ modified sorbents after longruns (left - longer calcination time, right - shorter calcination time)	64
Figure 47 SEM images of ZrO ₂ modified sorbents after longruns (left - longer calcination time, right - shorter calcination time)	64
Figure 48 Thermograms of sorbents prepared by modification with SiO ₂	65
Figure 49 Capture rate profiles of SiO ₂ modified sorbents during first (left) and last (right) cycle	66
Figure 50 SEM images of dry-mixed SiO ₂ modified sorbent (left) and using sol-gel like method (right)	66
Figure 51 Evolution of sorption capacity with increase of cycle number.....	67
Figure 52 SEM images of unmodified sorbent (left) and modified with 5% SrCO ₃ , after 23 cycles.....	68

List of tables

Table 1 Formation of calcium sulphur compounds with respect to conditions	31
Table 2 List of used reagents	39
Table 3 Melting and Tammann temperatures gathered, when compound is noted with *, it means, that initial modifier was carbonate, which decomposed during calcination as a preparation step, ** stands for quartz.....	40
Table 4 Results of surface analysis for each sorbent	43
Table 5 Dynamic sorption tests conditions	50
Table 6 Longrun test experimental conditions.....	55
Table 7 Gathered sorption capacities obtained for carbonate modified sorbents	57
Table 8 Gathered sorption capacities obtained for sol-gel like modified sorbents	62
Table 9 Gathered sorption capacities obtained for SiO ₂ modified sorbents.....	66

1. Introduction

According to World Energy Outlook developed by Energy Information Administration [1], world consumption of energy will increase by 48% in 2012-2040 period. This significant increase is caused by various factors, such as increasing world population and rise of the car numbers and electronic appliances used. Apart from the fact, that part of the energy produced worldwide is generated by renewable energy sources [2], fossil fuels and combustion will still play a significant role in global energy mix. Natural gas, crude oil derivatives, and coal are used for heat, electricity generation and as a transportation fuel. Currently, coal is still the most important primary energy source, powering power plants and for heat production. Increased energy consumption causes a problem with combustion products. Additionally, there still exists countries, like Australia, Poland and Turkey, which still want to extract coal and use it for energetic purposes [92]. All of the fossil fuels have the composition, which causes the presence of harmful gases such as sulphur and nitrogen oxides. Currently, world's biggest concern is carbon dioxide produced in enormous amounts during combustion.

Carbon dioxide is considered as the biggest contributor to global warming, which is affecting earth nowadays. From 18th century we can observe increased amount of carbon dioxide generation, caused by rapid development of industry all over the world. This fact, connected with the development of new technologies, availability of using electricity and increased interest in way of transportation are making a dramatic change to the environment. It is estimated, that from 1860, the temperature rose by less than 1 Celsius degree. Other symptoms of global warming are melting ice caps, the rise of the sea levels etc.

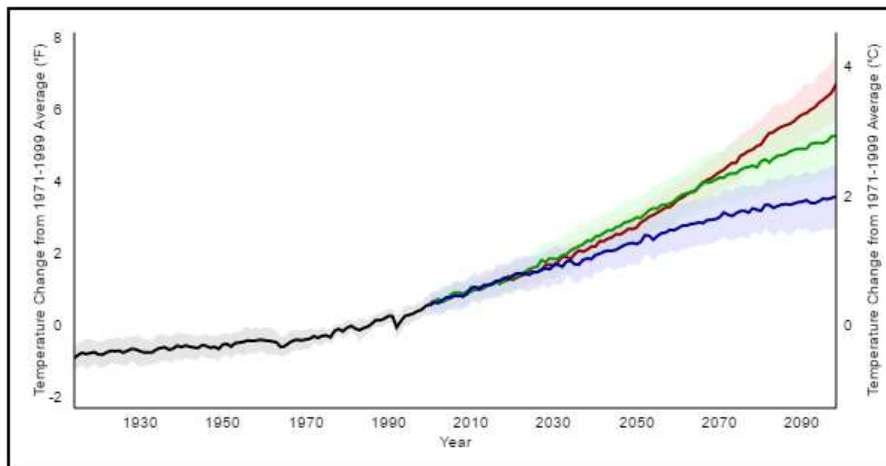


Figure 1 projection of temperature rise, according to National Oceanic & Atmospheric Administration[94]

IPCC in their report indicated, that global temperature rise is observed due to an increase of anthropogenic greenhouse gases concentration. This conclusion can be done when we observe a correlation between gases considered as greenhouse emission and changes of temperatures through time. In the year 2016 CO₂ level exceeded permanently level of 400ppm [91] and it can be linked with a continuous increase of average temperature in the world, which rises as well.

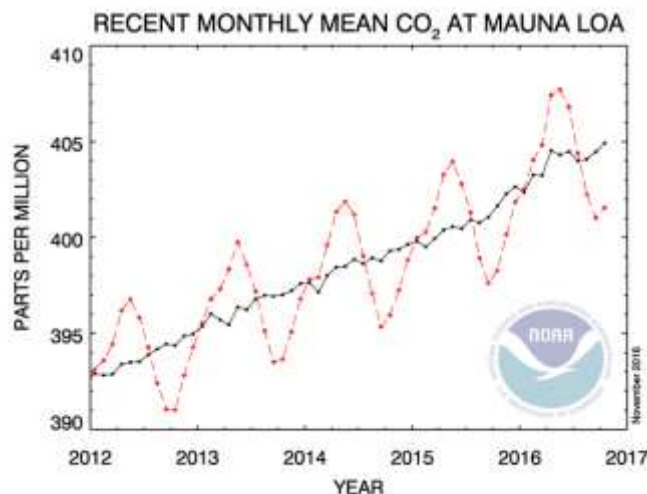


Figure 2 CO₂ concentration levels and temperature evolution observed at Mauna Loa NOAA observation point [93]

All of the evidences of global warming and its correlation with increased carbon dioxide emission tends to international incentives, which goal is to decrease emission of this compound to the atmosphere. One of the most important is Kyoto protocol. This document aims to stabilization of greenhouse gases concentration in the atmosphere by legal binding its members to help fight global warming. This treaty aimed to reduce carbon dioxide by 5.2% up to 2012. Making policies to reduce global warming and applying protocol principles is also an integral part of this treaty. It also wants an establishment of adaptation fund for minimizing impacts of global warming on people. It also involves regular monitoring of the policy including review, accounting and reports. This review system is like presenting the annual report at the completion of one policy cycle.

One of the consequences of Kyoto protocol is the origin of the emission trading system. It is the market-based approach to decrease emissions. The government gives permits to polluters equal to each participant baseline emissions, determined by historical emissions made. The goal is, that polluter needs to emit an amount of permissions which he has. In the case of bigger emission, he is forced to buy more allowances on a market. On the other hand, if the emission was smaller than the amount of permissions owned by a polluter, he can sell his permissions to third-party companies. In effect, the buyer pays a charge for polluting, while the seller gains a reward for having reduced emissions.

All of mentioned previously facts indicates, that carbon dioxide became a serious problem and there is a need to decrease carbon emission. One of the current subjects of research is carbon capture and storage technologies (CCS), which is considered to be technically feasible for industrial carbon dioxide emitters.

Objective of the thesis

The main goal of this work is to obtain stable sorbent made of cheap waste material. For that purpose, egg shells will be considered, as a waste material, which contains a high amount of calcium. The goal is not only to produce suitable sorbent, but also to find a suitable way to extend the capture capacity of the material, as well as the lifetime of the sorbent. To achieve this goal, various supports and preparation techniques will be examined.

Capacities of the sorbent will be examined by using them in multiple cycles of carbonation and calcination reactions. Experiments will also include adjustment in process conditions, in order to see its influence on results obtained.

Thesis outline

This thesis consists of five consecutive chapters. Apart from introduction, the second one is devoted to state-of-the-art review on Carbon Capture and Storage technologies, starting from basic concepts proposed, through various technologies and approaches from CO₂ sequestration, through transport and reaching final destination. Then, brief description of current investigated approaches to capture CO₂ from outlet gas streams is provided. Afterwards presentation of adsorbents suitable for CCS technologies usage is made. The last part of literature review is presentation of current knowledge about calcium looping cycle in details. Big attention has been paid on ways of pre-treatment of sorbents.

Third chapter is a description of sorbent preparation methods together with methods used to examine them, while the fourth one is devoted to discussion on results obtained.

The last chapter consist of conclusions based on results obtained, together with further recommendations and prospects for future work.

2. Literature review

According to the data of International Energy Agency, 68% of anthropogenic greenhouse emission is emitted because of the energy generation, both electricity and heat[4]. 90% of emitted gases is, in fact, carbon dioxide. This fact, connected with United Nations estimation on world population, which will reach 9 billion in 2040 [find source] and projected energy demand, which will increase by 37% in the same moment. Even if usage of renewable energy is still rising, humankind is not able to develop more energy without carbon dioxide emission. Currently, in global energy mix fossil fuels have a dominant part, more than 80%[5]. It means, that fossil fuels will still be an essential part of the energy mix.

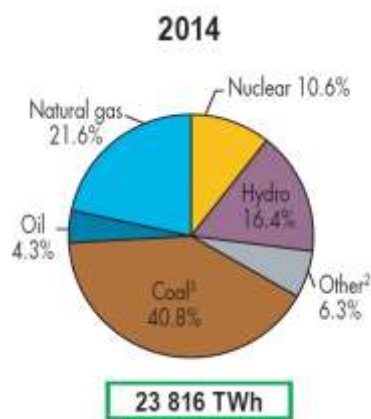


Figure 3 Electricity generation by source, according to International Energy Agency[5]

According to the current state of European energy market, we can unequivocally say, that coal will be still the primary source of energy in Europe, thus, will generate carbon dioxide. In order to prevent the environment from consequences, several incentives were established throughout the European Union. One of the most important was the plan to decrease emissions by 20% to 2020, with respect to 1990 emission levels.

All of the environmental issues and incentives followed by and regulations established by various organisations made an increasing interest in technologies of carbon capture and storage (CCS). The objective of the process is to avoid the emission of carbon dioxide to the atmosphere by using physical or chemical treatment, according to method's basis.

CCS

Carbon capture and storage, in general, are the techniques which prevent the emission of carbon dioxide to the atmosphere. Depending on a type of installation, we can distinguish 3 types of these technologies:

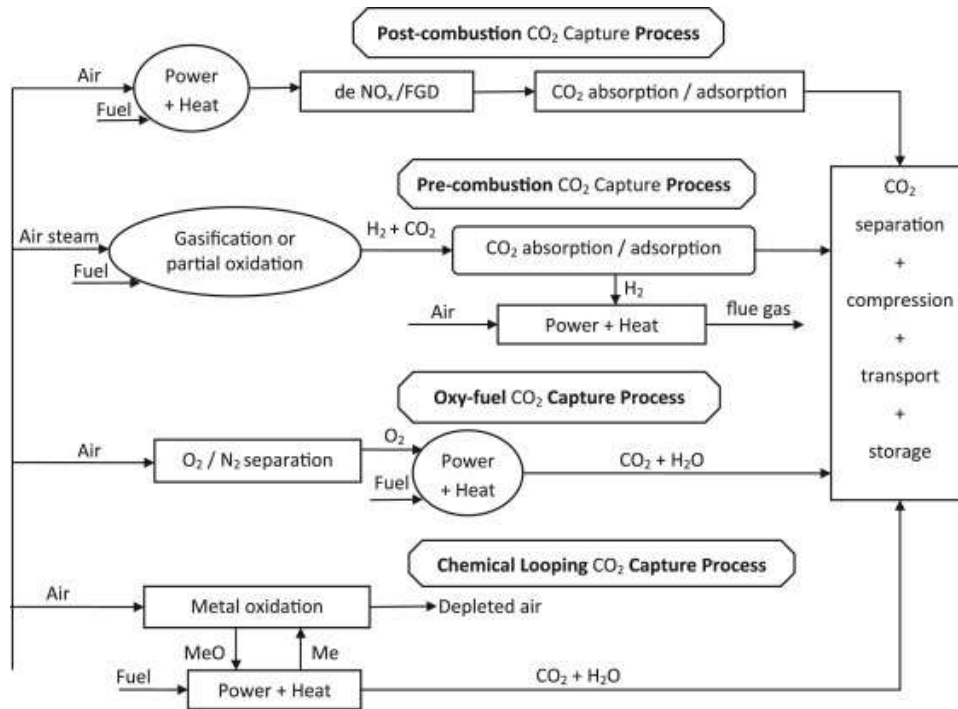


Figure 4 Available CCS technologies [95]

Pre-combustion capture

This technique can be used in the gasification process, when the fuel is gasified, which results in carbon monoxide and hydrogen as products. The method is strongly connected with the Water Gas Shift Reaction, which results in carbon dioxide and hydrogen, and hydrogen is the energy carrier for further combustion. The method results in a carbon dioxide stream which can be sequestered. The method can be used mainly in gasifying units, which were built especially for that purpose and it has almost no ability to be used as a retrofit one.

Oxy-fuel combustion

The method which assumes burning the fuel in a stream of pure oxygen instead of air. If the fuel is burnt without nitrogen presence, there is a significant reduction of fuel consumption; up to 75% and higher flame temperatures are achievable. The method results in the flue gas which consists of mainly carbon dioxide, which is ready for sequestration.

Post-combustion capture

Post-combustion capture is a technique, which separates carbon dioxide from exhaust gases after fuel combustion. There are several methods which work at different mechanisms, such as adsorption, chemisorption and cryogenic separation. Currently, it is the most extensively examined solution. The main advantage of post-combustion capture among previous two is the fact, that operation is taking place on exhaust gases after leaving the furnace. That allows to retrofit operating facilities and it has a bigger ability to adjust the whole process. Also, it does not need to change existing processes.

Additionally, there is a possibility of including capture process in a cleaning of effluent stream, what allows integration with power production.

Post-combustion capture is the most cost-effective in large carbon dioxide emitters, such as power plants or large industry facilities such as cement, steel and oil. Depending on a phenomena which are used for carbon dioxide sequestration, there are five ways to perform separation, which are:

Absorption processes

This kind of process is the most mature and popular commercial process, developed to industrial scale. In absorption processes, liquid sorbent is used to separate the carbon dioxide from the exhaust gases. Combustion products are cooled down and passed through other treatments (dust removal, desulphurization), then gas contacts liquid and carries carbon dioxide. After treatment, carbon dioxide is separated from the liquid, creating an almost pure stream for transportation. The sorbent can be reused after regeneration, which can be done by the regenerative process, such as heating or depressurization or by a stripping. Typical sorbents used in this technique are monoethanolamine (MEA), diethanolamine (DEA) and potassium carbonate.

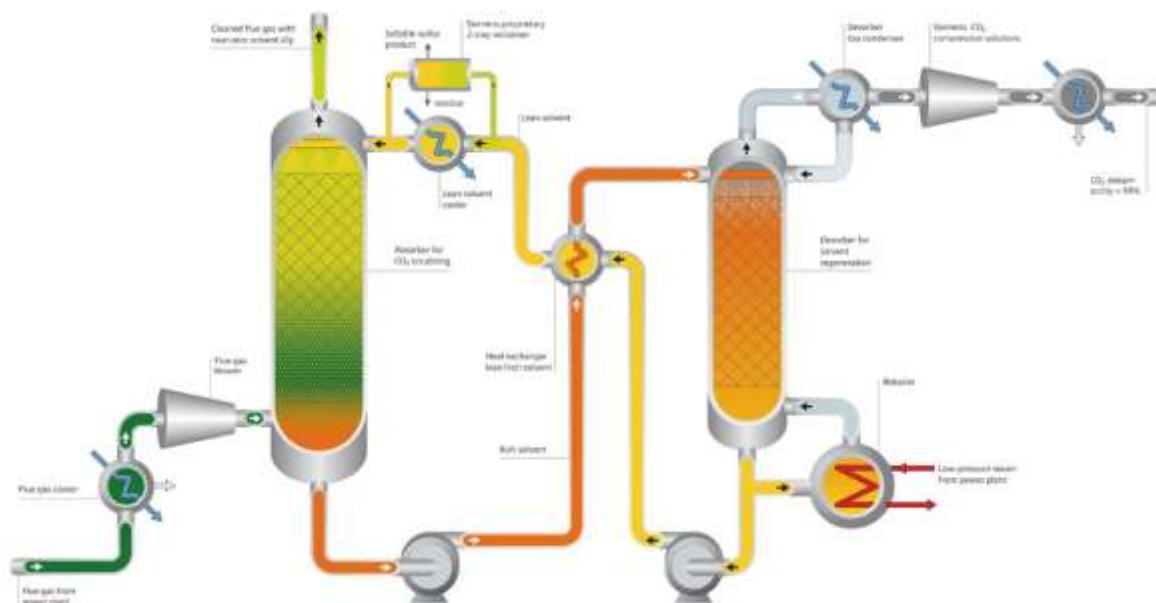


Figure 5 Absorption apparatus and process schematics [96]

As it was stated before, from all of the carbon capture and storage techniques absorption is the most mature one. It provides high absorption efficiency (around 90% of CO₂ removal). High regeneration ability also favors this method. However, the efficiency of this method highly depends on CO₂ concentration in the gas stream. Amine absorption technology is highly corrosive. Also, the method needs a significant amount of heat for sorbent regeneration, what increases energy penalty. The other problem is the disposal of spent sorbent, which is not harmful, but its decomposition products, such as nitrosamines and nitramines, which formation occur both in the gas phase and atmospheric aqueous phase, including water-containing aerosol particles and cloud-, rain- and fog-droplets, are toxic and

carcinogenic. Having that in mind, the environmental impact of absorption by amines and management of spent material is tremendous and all of the efforts to decrease their impact should be undertaken.

Currently, methods to improve the process are investigated. They focus mainly on finding alternative solvents, such as MDEA (methyl diethanolamine), which exhibits less usage of steam needed in regeneration step.

Another absorption agent which attracted attention with its properties and effectiveness is ionic liquid (IL). Its properties favour IL as an attractive sorbent because of its good thermal stability, high polarity, being non-toxic and a very low vapor pressure. IL can be used both as physical and chemical absorbent. The limitation which is currently investigated when considering IL separation is high viscosity, caused by hydrogen bond formation between cation and anion. To enhance CO₂ capture by IL, Zhang proposed to use the supported ILs [6]. Their researches indicated, that support made of silica gel helps to increase capture capacity from 0.2 to 1.2 mol of CO₂ per mol of IL. Reduction of the high viscosity of ILs effects following ones was mixed with alkanoamine. Additionally higher energy efficiency of the mixture was observed, as well as absorption rate and absorption capacity [7].

Cryogenic separation

Cryogenic CO₂ capture is a process, which removes carbon dioxide by means of cooling and condensation. The method is based on cooling CO₂ rich stream to temperature, in which it is present in the liquid state. Depending on the final temperature of the process, it is capable of capturing 99% at -135 °C and 90% of CO₂ at -120 °C. The process itself has many advantages, such as it is ready for transportation in liquid state, carbon dioxide stream is extremely pure. CCC has also a big affinity to use it as a retrofit technology both as integrated one. However, this method major disadvantage is energy consumption, which is high because of the cooling process.

Membrane separators

Membranes can be used for separation of CO₂ from flue gas stream. The essential part of the separation is a membrane, usually made of composite material and supported by a non-selective layer which provides mechanical support to the membrane itself. The efficiency of the process which can be achieved is around 82 up to 88%. Currently, there are ceramic and metallic membranes under development, which can exhibit a bigger efficiency of the capturing.

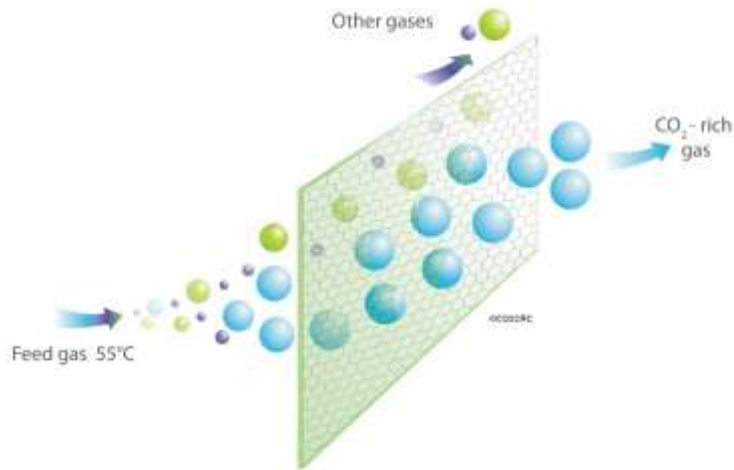


Figure 6 Membrane separation scheme [10]

Membranes are often considered as a method with the best future prospects, however, there are still challenges which need to be taken into consideration [9][10]. The most important limitation which needs to be overcome is dealing with diluted CO₂ stream, which favors lower efficiencies of the process. The same situation is with flue gas pressure, which needs to be high enough to create pressure difference in order to perform membrane separation.

Biological treatment

One of the investigated ways to perform CO₂ capture is to use microorganisms, such as algae[12]. The method bases on cultivation of microorganisms using by-products of large-scale fossil fuel combustion as in the case of the power plant. Algae are the most interesting organisms to perform CO₂ capture because of its special features. They are performing photosynthesis, what is crucial for CO₂ capture and they can be satisfied with small amount of nutrient. The process can be done in two types of reactors, ponds or tanks with algae or in specially designed photobioreactors. Ponds are considered as a less effective, but also with smaller investment and maintenance and operation costs.

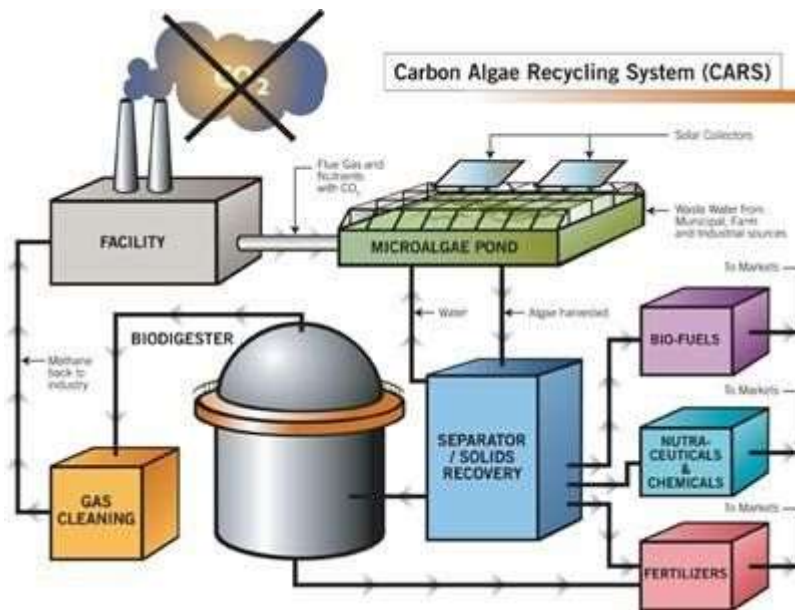


Figure 7 Proposed model of microalgae usage for CO₂ capture[97]

Usage of microbiological treatment is considered as a very expensive way to capture CO₂, however, there are some researches done to make the process more economically feasible. One approach assumes usage of grown algae as a biodiesel feedstock [11], when algae are considered as the best substrate to produce this fuel comparing prices and ways of treatment.

One of the other issues is, that photosynthesis is possible only during the day, because of the sunlight, which is an essential to perform the process. One of the approaches applied to overcome this problem is the usage of a closed-loop consisting of bicarbonate/carbonate recirculation, where bicarbonate is a CO₂ sorbent and a pond with alkaliphilic cyanobacteria culture, which is responsible for bicarbonate regeneration [13]. This method can avoid problem of no CO₂ capture during lack of sun and can obtain reasonable results with the efficiency.

Adsorption systems

One of the most developed methods, which is currently under investigation and can be considered as the most promising one is the usage of solid sorbents, which use adsorption phenomena. Amine absorption process, which is the most developed one, however, it has some disadvantages such as low loading of carbon dioxide, the small contact area between the gas and liquid phase as well as being a corrosive agent[14]. Because of that, solid adsorption could be a real alternative for carbon capture.

Adsorption processes are the ones which work on gas-solid interactions. Solid material adsorbs carbon dioxide in certain pressure or temperature on a surface. Next step is a regeneration of sorbent and reuse in the following cycle. There are two ways to regenerate sorbent, one is TSA, temperature swing adsorption, which is done by increase of temperature, PSA, pressure swing adsorption, in which adsorption is done by the change of pressure, electric swing adsorption, where adsorption and desorption are done by electricity supply and low-voltage current passing through adsorbent and vacuum swing adsorption (VSA)[15].

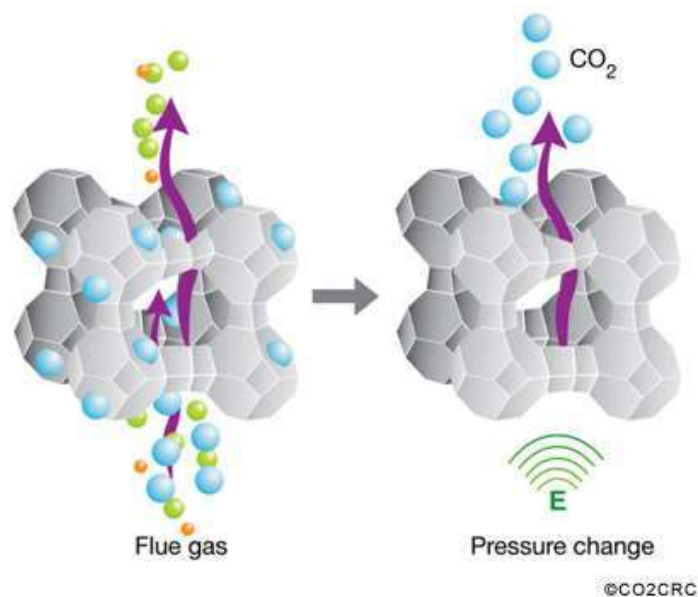


Figure 8 Adsorption with PSA

Taking into account materials, the usage of materials with the big surface area is desirable, such as micro or mesoporous materials, activated carbon, zeolites, metalo-organic frameworks MOF and metal oxides. All of the mentioned materials are able to capture both CO₂ and SO₂ simultaneously. Also, their regeneration has a low cost. The main advantage of adsorption is accessibility to materials, which are common and reasonably cheap.

The main disadvantages of adsorption process are sintering and thermal stability. After several cycles, the material is becoming more and more sintered, what decreases significantly. That is why currently the main focus is on develop material, which will be thermally stable and there would be a possibility of sintering reduction. Moreover, heat released by the exothermic reaction is very high in a solid system, what creates problems with an operation which should be overcome before afterward development [16].

CO₂ transportation

After carbon dioxide is captured it needs to be transported to the site when it can be stored. Transport of CO₂ can be done in all of the three states of a matter, so that liquid, solid and gaseous state. Currently, commercial scale transport is performed by tanks, pipelines and ships for gaseous and liquid ones.

One of the most important factors concerning CO₂ transportation is compression of volume to transport it. Because of the fact, that solidification needs a significant amount of energy because of the cooling down the CO₂, transportation is done in other states. Ways of transportation are pipelines, ships or road tankers [17].

CO₂ storage

The last point of CCS technologies is sequestration of carbon dioxide. There are three proposed ways to sequestrate CO₂, in geological formations, deposited in deep ocean water – so called ocean storage and in mineral carbonate form, known also as mineral storage.

Deep ocean storage might influence ocean acidification, what is another issue to take into account globally. Because of that, geological formations are currently considered the most promising sequestration sites.

Storage in deep geological structures, known as 'geo-sequestration', bases on carbon dioxide conversion into supercritical CO₂. This stream is then sequestered into sedimentary rocks. Their presence can occur in old oil fields, gas fields, or in saline formations. Other suggested storage sites are unminable coal seams and saline water-filled basalt volcanic rocks. Various physical, e.g. impermeable 'caprock', and geochemical bonding mechanisms makes CO₂ escape to the surface impossible.

The main difficulty in terms of depleted oil fields usage is their geographical distribution, which can affect costs of operation, since their limited capacity cannot be ideal for this purpose. Also, combustion of recovered oil through enhanced oil recovery will cause additional CO₂ emissions.

Unminable coal seams might be used to store CO₂ because of their permeability in respect to CO₂ and, additionally, costs of excavation makes the process unprofitable, or even in some cases impossible to extract deposit. CO₂ is replacing then another gas present in coal deposits – methane, which can be extracted and then used in similar manner as other fossil fuels. The process proposed is called ECBM and stands for enhanced coal bed methane. The sale of the methane can be used to decrease slightly the cost of the CO₂ storage. However, as in EOR, combustion of extracted gas would also produce CO₂ which would cause benefits of storing the original CO₂ reduction.

Some deep rock formations contain highly concentrated brine which is present in the rock pores and have so far been considered of no benefit to humans. In the past, they have been rarely used for storage of chemical waste. However, the value of saline aquifers is again investigated. Their main advantage for CCS is their big storage volume and common occurrence. As an example, much of the North Sea and Baltic Sea, together with the Texas Gulf Coast is underlain by large saline aquifers. Their main disadvantage is small knowledge about the structure itself, together with no additional product obtained during the process, which will possibly decrease cost of operation

In mineral storage, captured CO₂ is reacted with naturally occurring magnesium and calcium containing minerals. This is called mineral carbonation and occurs naturally as the weathering of rock over geologic time periods. The problem regarding this way of CO₂ storage is, that carbonation processes are very slow in normal conditions, thus additional energy is required to immobilize CO₂ [18].

Economics of CO₂ capture

Generation of energy is closely connected to the efficiency of a power generation. Not all of the calorific value of fuel used is the process of combustion, usual efficiency of a boiler lies within the range of 25 up to 50% [45]. One of the goal to achieve considering CO₂ emission reduction is to increase efficiency, what causes higher electricity generation with the same amount of CO₂ emitted. The operation of CCS technology is strongly connected with energy consumption in order to perform the process. The operation of CO₂ capture, together with pumping during transportation and storage, as well as in most of the cases regeneration of sorption material, all of that tends to decrease of energy generated what is

called energy penalty. This particular term refers to losses caused in a power plant by installing CCS technology in the facility and covers all of the energy requirements for electricity and thermal energy [44]. Energy penalty, used by IPCC, can be calculated by the difference of plant efficiency with CCS in respect to reference efficiency without CCS installation, according to equation presented below.

$$\Delta E = 1 - \frac{\text{Efficiency of plant with carbon capture}}{\text{Efficiency of reference plant}}$$

Energy penalty is one of the main issues concerning Carbon Capture and Storage technologies. Considering all of the proposed solutions to capture CO₂, all of them are consuming a significant amount of energy. However, all of the technologies which are investigated have their advantages and challenges to face.

In the case of the first ones chemical solvents are capable of providing rapid kinetics, what allows to minimize CO₂ partial pressure and heat exchange can be done much more efficient in a liquid phase which is actually in use. However, this type of operation involves a large amount of steam for solvent regeneration, as well as the energy required for further operations on non-reactive carrier liquid. All of that can tend to decrease of efficiency by 10% comparing to plant without MEA solvent systems [46].

On the other hand, technology based on solid adsorbent is providing bigger capacities even with smaller amounts of materials used, however, managing solid system is much more complicated comparing to wet-scrubbing ones, what can create operational issues, as well as bigger pressure drop in a system.

Energy penalty is one of the most important issues to overcome during the development of CCS technologies. Currently is one of the most important ways to make the process more efficient and developed and should be the real concern when implementing to power plants.

Review of adsorbents used in CO₂ capture [19]

As it was mentioned before, adsorption processes are based on solid dry sorbents, which are capable of capture carbon dioxide selectively from a gas stream. Key properties of used sorbents are surface tension, pore size, process conditions, which depends on a method, in particular pressure or temperature. Adsorbents can be divided into three groups, which are inorganic adsorbents, organic adsorbents and hybrids, which are composed of both inorganic and organic compounds and bonded.

Zeolites

Term zeolite usually refers to the materials, which are crystalline hydrated aluminosilicates with framework structure. They consist of three-dimensional polyanionic networks made of SiO₄ and AlO₄ tetrahedra. All of the structures are linked by oxygen atoms[20]. However, the exact definition is still under development [21]. The term zeolite is derived by Cronstedt in 1756 from two Greek words, zeo, which means to boil and lithos, stone. This type of material exist as a natural material, however, their increased importance can be observed after industrial scale availability in the 1950s. Zeolites consumption for various applications, such as adsorbents for separating and purifying substances and also as catalysts or ion exchangers for water treatment.

Taking into account structure of zeolite, they can contain both channels inside or interlinked voids. Chemical and physical properties are determined by the aluminum content in frameworks. Because of that, one of the most important parameters of zeolites is Si/Al, or $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. The higher ratio is, the lower ion-exchange capacity of zeolite can be achieved. Zeolites are widely used as an adsorption agent because of the molecular-sieve effect, which is caused by regular pores with definite aperture sizes. This helps with separation of two different molecule sizes. This is why adsorption efficiency of zeolites highly depends on the size of a structure, but also on charge density and chemical composition of cations present in porous structure[22]. Zeolites potentially can be used for CO_2 capture using PSA process, however, their selectivity in flue gas stream is still at relatively low level[23].

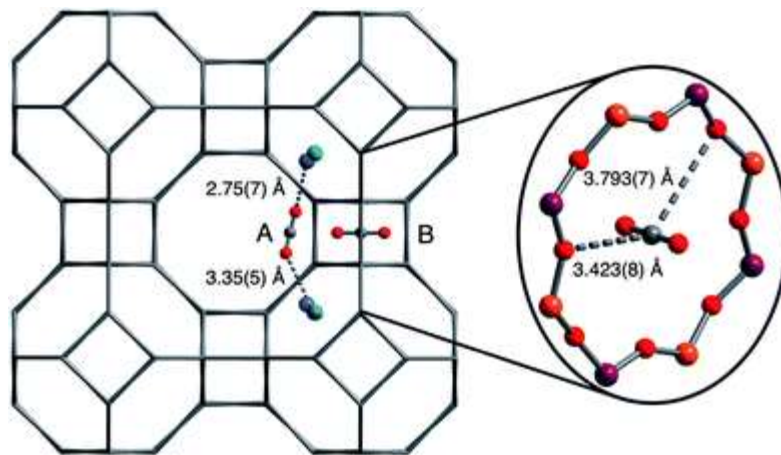


Figure 9 Zeolite schematic structure

A number of zeolites were examined in terms of its CO_2 adsorption features. Mainly investigated were highly crystalline materials, which have high surface area. According to Harlick et al. [24], after studying 13 zeolite-based adsorbents determined the important adsorbent characteristic, which is low $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and presence of cations with high electrostatic interaction affinity with CO_2 .

Apart from low production costs, as well as the mild condition of maintaining the process, zeolite as an adsorption agent has several drawbacks. As it is reported, the zeolite can adsorb moisture easily, what affects CO_2 capture results. Water present in the stream is not a favorable condition for CO_2 capture as well [33]. Also, desorption of CO_2 from material needs a significant amount of energy, what is caused by VSA process and makes this process economically unfeasible [25], however, there exist a possibility to use waste heat from the processes to perform regeneration through TSA, what can make the process cheaper[28]. Another comparison of materials named 13X and 5A described in [29] indicated that in terms of using TSA and zeolite 5A is the better one for this type of adsorption-desorption cycle applied.

Current researches done on the field of zeolite application in CO_2 capture focus on exchange alkaline-earth and alkali cations. The idea is to change electric field as well as the pore volume available for the capture inside. [30] shows the effects of exchange Li, K, Na, Rb and Cs on Y and X zeolites and the result was the most promising with zeolites which contained lithium, what presumably can be explained by a bigger interaction of CO_2 with smaller atoms such as Li. On the other hand, in [31] cesium with Y zeolite exhibited promising result in desorption in higher temperatures, while [32] reported higher thermal stability of Ba with zeolite ZSM-5 among Li, Na, K, Rb and Cs.

Metal-organic frameworks (MOFs)

One of the materials which cause increasing interest in terms of the CO₂ capture is Metal Organic Framework, MOF. This material is made of metal ions connected between themselves with organic ligands. This construction material is capable of form two and three-dimensional structure connected with strong bonds, which allows forming crystalline, porous framework, which can remain unaffected[26]. MOFs exhibited enormous potential for CO₂ capture and storage. The other advantages of that material with a comparison to traditional adsorbent material such as activated carbon, silica and zeolites are high crystallinity with well-defined pore structure, easy adaptation to the role of the material, including CO₂ capture. One of the most extensively examined applications of MOFs is storage of various gases.

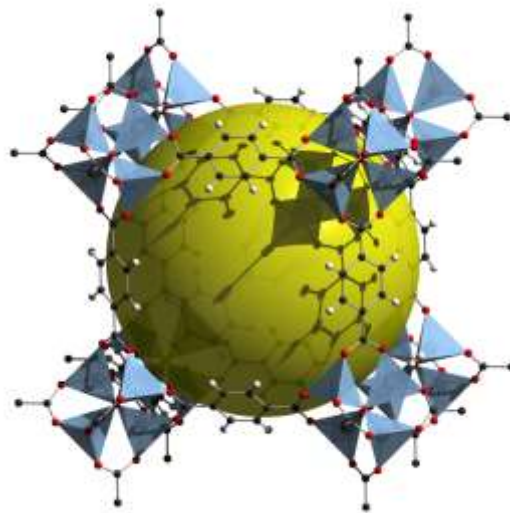


Figure 10 MOF-5 structure [33]

When It comes to carbon capture and storage technologies involving MOFs, there are several obstacles to overcome during the development of the material [33]. One is the selectivity with respect to CO₂. Its presence in flue gas outlet is minor, giving a place for other molecules such as nitrogen, water and O₂. Also, costs of production, as well as the development of a method to desorb captured CO₂ should be taken into consideration. To enhance the CO₂ adsorption three strategies were chosen: Incorporation of unsaturated metal centers (UMCs), metal doping and chemical functionalization.

Silica materials

Order mesoporous silica (OMSs) are the materials, which base on silica compounds are grafted with hydroxyl groups. This kind of modification allows to design pore structures specifically for capture certain compound and offer an additional surface area to increase the efficiency.

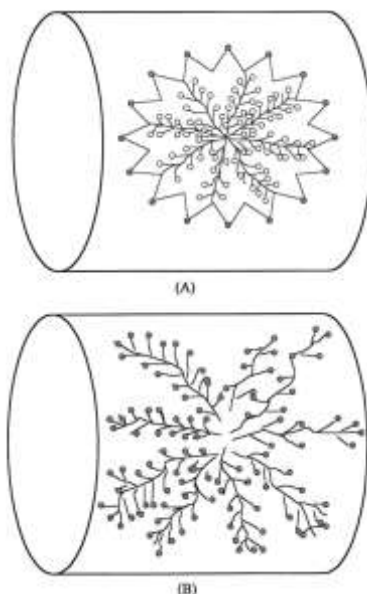


Figure 11 Molecular basket concept, dots are representing capture sites [36]

For CO₂ capture one of the most interesting concepts is to use polyamines, which possess high amine group density, which is crucial from amount of sorbed compound and slower adsorption/desorption kinetics [34]. The affinity of CO₂, which is Lewis acid, is high for basic amine sites. The concept is called “molecular basket”, which corresponds to double effect of CO₂ capture with a nanoporous silica support and polyamine, in particular in case, when loading of polyamines is high. In a paper written by Du [35] results of CO₂ uptake on nano-silica with polyethyleneimine showed remarkably high sorption at the level of 3.8mmol/g of adsorbent at 100 kPa pressure and 40 °C. The other interesting properties of the material were rapid adsorption rate, the good selectivity of separation in respect to N₂, as well as easy regeneration of the material. The advantage of amine grafted materials among zeolites was also the fact, that increase of temperature had not decreased uptake as in the case of zeolitic materials. Also, regenerability of molecular basket sorbent is relatively high, after 10 cycles 92% of sorption capacity was still available [36].

Activated carbon

Name activated carbon refers to materials, which can be characterized by pores of various sizes in the range of submicropores up to macropores [20]. When it comes to feedstock for activated carbon, it can be almost all of the carbon-containing materials, such as coal, nut shells, wood, oil products etc. The process of activated carbon manufacturing consist of two phases, one of them is carbonization of the material, where the raw carbonaceous material is partially pyrolysed. The second phase is activation, which can be done by two means, chemical and gas activation. The chemical method basis is the usage of certain substances, which role is to dehydrate material. Usually, the process is maintained in the temperature range of 400-1000 °C. After treatment, chemicals used are removed by the means of extraction, what results in obtaining porous and active carbon structure. The second method is gas activation, in the temperature range 800-1000 °C. This method uses a stream of gas with combined oxygen in compounds like steam or carbon dioxide. At this conditions, decomposition of carbonaceous

material is happening, producing fine pores and cracks. All of those materials were considered as really efficient ones then it comes to gas streams purification from various compounds, such as carbon dioxide.

Currently, activated carbons have a wide variety of application in adsorption agents. Most widespread one is water treatment, where it is used as a dechlorination agent and for removal of other harmful compounds, such as aromatics, pesticides, and bisphenol A. Activated carbon is also used for flue gases treatment, they can be successfully used as a sorbent for VOCs as well as heavy metals.

Chemical characteristics of activated carbons are highly connected with the degree of surface chemical heterogeneity, caused by the presence of heteroatoms present in activated carbon structure, which can be oxygen, nitrogen, hydrogen, sulphur and phosphorus. Presented atoms have an influence on the character of a surface, which can be basic or acidic, and highly influence sorption capacities. In fact, the basic surfaces on activated carbon, which usually corresponds to resonating π -electrons of carbon aromatic rings or for basic surface functionalities caused by nitrogen containing groups are beneficial for CO₂ capture [38]. This is why the main efforts which are currently done to improve activated carbon sorption capacity is a removal or neutralization of acidic functional groups present on a surface or replacing acid group with basic ones.

One of the proposed ways is to use heat treatment of a sorbent. At higher temperatures in the range of 800-1000 °C and in presence of inert atmosphere, it was found out, that majority of oxygen functional groups were decomposed and thus in place of acidic groups, there are unsaturated surfaces [39]. However, the method exhibits limitation to the temperature of 1000 °C and as a result, the material obtained has a low degree of activity.

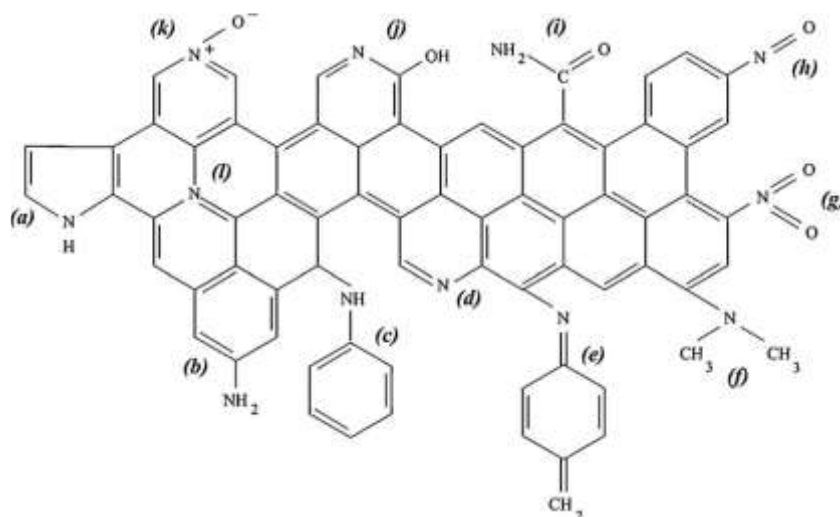


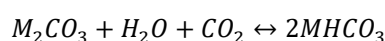
Figure 12 Nitrogen surface active groups on activated carbon [39]

Another way to improve CO₂ adsorption is the treatment of activated carbon by ammonia. Ammonia grafted activated carbon increase basicity. The observed mechanism of such pretreatment of an adsorbent leads to decomposition of ammonia and then reaction with carboxylic acid sites to create amides and nitriles. Another reaction which can be observed is the formation of amines by substitution hydroxylic groups.

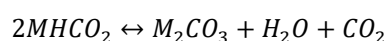
Generally speaking, activated carbon can be considered as a promising material for CO₂ capture, however, usage of that method tends to some difficulties which need to be overcome. One of the most important is relatively low selectivity of the material, what gives low CO₂ intake. Also, process conditions favor bigger pressures, what increase the amount of energy needed for a process. However, a big abundance of a raw material, as well as high regenerability of the sorbent are the strong points, which favors further research on that type of material.

Alkali metal adsorbent materials

Alkali metal adsorbents are carbonates of metals, which belong to the first and second group on PTE. Metals carbonate are then supported on one of the inorganic supports, such as zirconia, ceramics, silica or alumina. Sorption is taking place between the material and the moisture, where carbonation occurs, then decarbonisation is happening according to scheme presented below



M stands for Na and K, ΔH for their hydrocarbonates are -135 and -141 kJ/mol respectively



The reaction presented normally occurs in the temperature range at 333-383K, while the regeneration occurs at 373-473K, when CO₂ is released. Theoretical adsorption capacity can be up to 41.5% for K₂CO₃ adsorbents [19]. One of the biggest advantages of this process is the possibility of sorption in wet condition, what is really important when taking into consideration composition of a flue gases, which mainly consist of nitrogen, CO₂ and water. The another advantage of other techniques is also a fact, that regeneration is taking place at a relatively small temperature and can be done under atmospheric pressure, what gives an opportunity to make the process economically feasible. However, real yield of uptake, which usually lies between 3 up to 11% and continuous decrease of collection ratio, caused by the formation of stable products such as hydrocarbonates or hydrated carbonates is a real issue. The another problem which can be considered as a major is the influence of other compounds present in flue gas stream. It is predicted, that big potential effect would have chlorides and sulphates, which can form stable sulphate (IV), (VI) and chlorides [40]. In [41] effect of SO₂ was studied, with 0.1-0.2% trace in the gas mix during TGA analysis. Continuous sorption determined, that after several cycles sorption capacity was decreasing because of the formation of Na₂SO₃, which does not decompose at temperatures which were used during the process. However in [42], when K₂CO₃ supported on Al₂O₃ was investigated, the material exhibited good sulfation resistance after H₂O pretreatment.

Current researches concerning alkali metal based dry adsorbents are taken in two ways. First is to develop sorbent, which will be attrition resistant and its kinetic properties need to be known well. Currently, state of the knowledge about alkali metal carbonates limits to the pure material without the support. The second way is the process development to make it more technically feasible. More and more researches should be done in order to understand the influence of the impurities which can appear in the flue gas stream. Also, improvements in general process integration should be investigated, in the

fields of the heat integration, the load capacity of sorbent, the low-pressure drop across the whole system and usage of lower pressure of steam in regeneration.

Calcium oxide - carbonate cycle

Basis of the process

One of the processes which have an increased interest in carbon capture and storage technologies is Calcium Looping Cycle. The rapid evolution of calcium sorbents is caused by a fact, that scaled up technologies similar to that were already developed in large scale in fluidized beds. The another advantage among other sorbents is high abundance in the environment. Calcium is the fifth most common element in the earth crust, and calcium carbonate is the most common form of its presence [43].

The method is performed on a calcium oxide (CaO) as an adsorbent which reacts with carbon dioxide according to following reversible reaction:



The carbonation reaction is exothermic, while second step, calcination of a sample is endothermic one. Carbonation process is a treatment of the calcium oxide with a flue gas. The process is usually maintained at a temperature of 650-850 °C. The resulting material is a calcium carbonate. Calcium carbonate treated by higher temperature in the range of 850-1000 °C decomposes into CaO and CO₂, creating a stream of clean carbon dioxide and sorbent available for reuse.

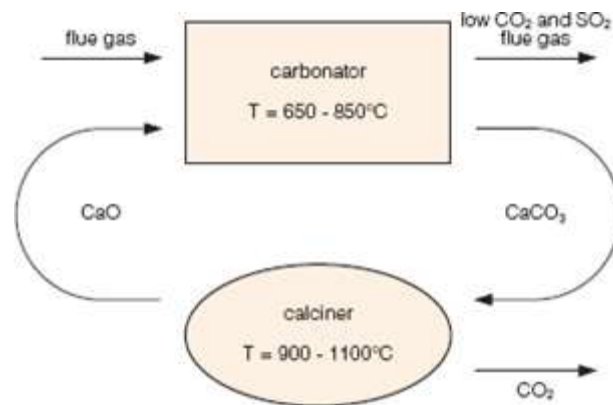


Figure 13 Scheme of carbonation – calcination process in Calcium Looping Cycle application[98]

There are many investigations of calcium oxide sorbent kinetics, specific for both phases, so that carbonation and calcination. For carbonation process it is known, that reaction between calcium oxide and carbon dioxide occurs in two regimes. The first stage is fast and gas-solid reaction is taking place on the surface, where the layer of CaCO₃ is formed. As the formation of carbonate proceeds, the rate of reaction decreases due to the diffusion limitation of reacting species through the new surface created [44]. When specifying conditions for carbonation, there is a need to balance it between high

temperatures, which are causing the higher speed of the reaction, and lower ones, which favours equilibrium conversion in that process.

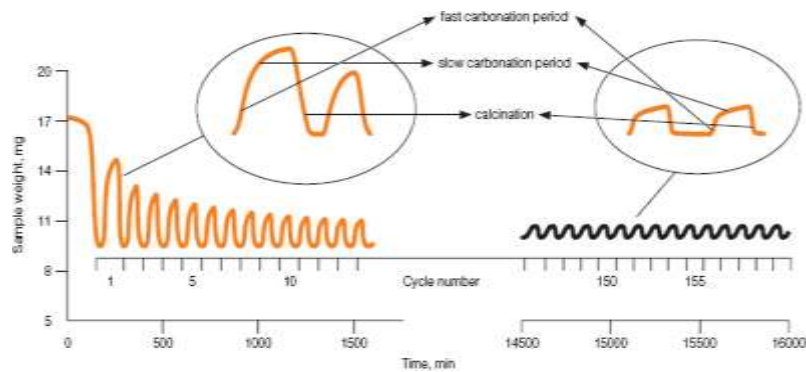


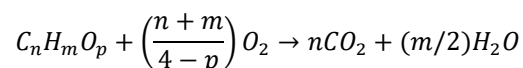
Figure 14 Calcination and carbonation presented in cycles [98]

Calcination process of a sorbent spent on CO₂ capture can be done using reversible reaction for carbonation. This reaction is endothermic, so it is favored by higher temperatures than carbonation. Usually, the process is maintained in the temperature range of 900-1100 °C. The reaction is favored by higher temperatures. One of the major issues regarding is partial pressure of CO₂ above the solid surface of carbonated material [47]. Also, it may happen, that high CO₂ concentrations can be observed in pores of a particle, what leads to inhibition of a process as well. The most important effect of CO₂ presence is a reduction of surface area and an increase of the average pore diameter [48].

During calcination/carbonation cycle one may observe a decrease in weight of the sample during next stages of a cycle. It happens because of the attrition of a material used, as well as sintering of pores present in the fresh sample. The another issue is, that during carbonation CO₂ reacts more likely with the outer surface of CaO instead of pores inside, what leads to pore closure and decreased carrying capacity of a sorbent [49].

Precombustion application

The main goal of pre-combustion processes is to produce hydrogen from a carbonaceous source. All of the processes involves several reactions taking place in gasifier units, what can be presented using following reaction scheme:



CO₂ capture can be done without respect to material gasified, as it was investigated for steam-methane reforming [50], coal gasification [51] and biomass gasification as well [52]. The reaction of CaO with CO₂ is performed in situ, simultaneously with other processes performed in gasifier, so pyrolysis, partial oxidation of a coal and water-gas shift reaction (WGS). The remaining CO₂ present in gas created during the reaction is then captured by particles of adsorbent. Since WGS is equilibrium reaction, capture of CO₂ is causing change of equilibrium inside the reactor and favours bigger amount of H₂ created during the process. The scheme of equipment used for gasification with CO₂ capture coupled is presented at

figure [figure 6 from 52]. The looping of the calcium material is also providing opportunity to use heat used for calcination of material with CO₂ adsorbed.

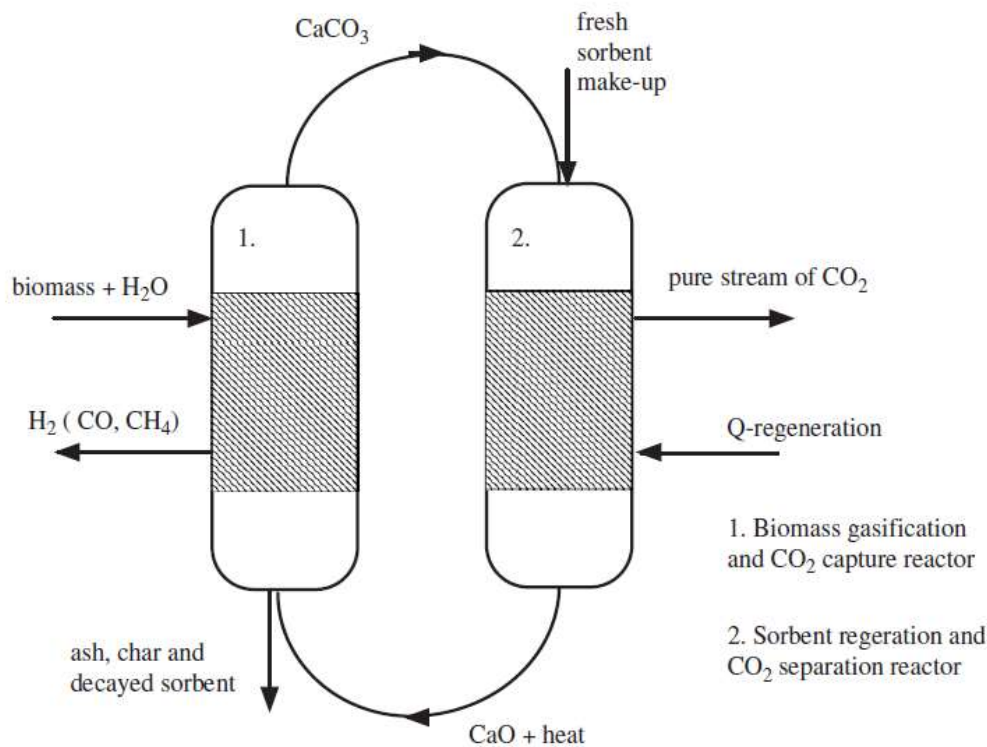


Figure 15 Schematics of Precombustion Calcium looping cycle application for biomass gasification [52]

The results of using calcium oxide as a sorbent are highly beneficial for gasification of carbonaceous materials. According to [51] in investigation of the process it was found out, that in gas outlet was present from 71, up to 76% of H₂ for coal gasification and up to 95% of H₂ when it comes to biomass [52]. The process seems to be not favourable for steam-methane reforming, yielding 40-50% of hydrogen present [50]. Also it was determined, that using calcium sorbent increases significantly amount of carbon monoxide reacted in the mixture, resulting presence in gas outlet on the level of less than 2%. Removal of CO₂ lies only in very satisfactory results, since almost no carbon dioxide was present in gas outlet.

One of the issues regarding use calcium sorbent in pre-combustion technologies involving the presence of water in the gas phase. In the case of elevated pressure of H₂O, CaO is expected to form Ca(OH)₂ during the reaction with steam. However, equilibrium pressure of CO₂ is significantly smaller than H₂O, thus, there is much higher equilibrium driving force for CaO reaction with CO₂ rather than H₂O. On the other hand, it may happen, that some fractions of CaO applied to the process will be consumed to form calcium hydroxide. The other problem which may occur during especially biomass conversion is the presence of tar and coke, what can decrease sorbent carrying capacity. However, the mechanism of that sorbent deactivation is not well understood yet. Also, important thing is to find appropriate pressure of the process, which would not favor creation of calcium hydroxide in the case of too high, but sufficiently big to avoid the presence of CO and CO₂ in the outlet.

End of Pipe application

One of the most common applications of CaO sorbent for CO₂ capture is the usage in post-combustion so that the process is applied to the flue gases which are leaving boiler. Typical composition of flue gases from combustion is 66-76% of N₂, 6-14% of O₂, up to 14% of steam and 7-12% of CO₂ [53]. As it was determined in [54], we can distinguish 5 different schemes of using CaO as a sorbent.

The basic one assess limestone-derived sorbent captures CO₂ from flue gas in fluidized bed carbonator, which works within a temperature range of 873-923 K. Reacted sorbent is then passed to second fluidized bed reactor, which is performing the calcination at a temperature range, which is 200 K higher. To provide heat for the process in [55] was proposed to use coal in the calciner, burnt in CO₂ and O₂ atmosphere. Oxy-combustion is necessary in that case to maintain high CO₂ concentration to perform adsorption so that Air Separation Unit (ASU) is needed. As it was presented in [54], calculated energy penalty for that kind of operation lies in the range of 6 up to 8%.

The second way is to use direct heat transfer between combustion chamber and calciner. This method includes a lower temperature of calcination and steam used in order to decrease partial pressure of CO₂. However, if this process will need to be more efficient there is a need to make a great technological advance. The way how to improve the process is the usage of solid heat carrier, which is the third method. For heat exchange solids are used as for example spent sorbent or Al₂O₃, but this method can cause the problems with deactivation of sorbent and, in the case of another carrier, will include the process of separation of sorbent from inert species.

One of the methods, which works especially good with biomass sources, is to perform carbonation inside the combustion chamber. The basis is similar to one applied in gasifiers, but instead of producing hydrogen, the fuel is burned in air atmosphere causing total conversion of carbon to CO₂. The process in that regime can be performed in lower temperatures, additionally, unburnt particles of fuel are carried over to calciner and then combusted in rich O₂, present on that stage.

The last option is to use similar combined combustor/carbonator reactor, but with high-pressure and high-temperature in a fluidized bed. The whole point of integration in one combustion chamber allows to achieve higher efficiency, however, there is some significant disadvantage of maintaining the process in that conditions. One of the most important is the presence of sulfur in the combustion chamber. The presence of sulphur is causing sorbent deactivation due to calcium sulphate production. Also, there is a need to take into account effects of ash fouling during combustion. However, usage of that method of the technology application there is no necessity to install separate desulphurization unit, all of the sulphur oxides are captured and flue gas is free of these harmful compounds.

All of the application schemes are using heat generated during carbonation reaction in order to drive steam cycle, what results in producing additional power. When it comes to integration of the whole system there is a possibility of having significant energy savings, especially taking into account cement industry in which exist the opportunity to cultivate spent sorbent, what can increase profitability of both energy generation and cement production, which is also considered as energy consuming and significant CO₂ emitter due to the calcination of CaCO₃, which is performed in that type of facilities.

Sintering and attrition

One of the biggest problems of CaO sorbent technologies is highly connected with degradation of materials' surface due to attrition and sintering processes. Both of them are responsible for the decrease of the active surface on the sorbent, what leads to lower sorption capacity, thus process efficiency is lowered. One of the main directions of current researches is, in fact, lowering the impact of these phenomena during continuous processes.

Sintering in the case of CaO sorbents refers to coalescence of the material as a result of interaction between particles. Other effects of sintering are changes in pore shape, its shrinkage, and growth of material grains. This process is observed at higher temperatures and it is temperature dependent, but also of a composition of a gas [60]. As it was stated in [61] both CO₂ and H₂O have catalytic effects on CaO sintering. Sintering can be also explained by changes caused carbonation, which results with a bigger particle of CaCO₃, what continuously influences increase of grain size. As it was stated before, the temperature has a serious impact on particles sintering, in the temperature range of 700 °C it is slight, while in 1100 °C it can have a dramatic effect, causing almost complete sintering of a particles [62].

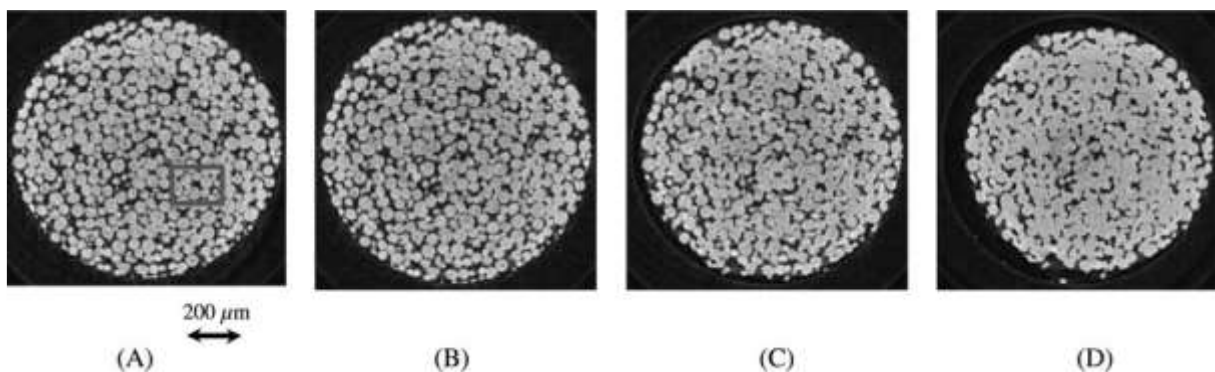


Figure 16 Sintering of particles [99]

Sintering of particles is leading to decreasing of sorption capacity during next cycles. This phenomenon decreases significantly the availability of pores, as well as the superficial area. As it was presented in [62], the biggest tendency to sinterization among CaCO₃, Ca(OH)₂ had limestone, due to the presence of other ions in natural rocks, what tends to irregularities in crystalline structure which may occur in higher sintering rate.

The second phenomenon which highly affects sorbent performance caused by surface degradation is attrition. It is the process particles are breaking up themselves, as well as a decrease of pore network present of each particle. In [63] it is claimed, that particles size affects extensively carbonation rates, but there is no possibility to find a general correlation between them, dependence is indirect. In the case of porosity, it works in a similar manner: higher porosity – higher sorption capacity, thus, higher CO₂ uptake.

Particles of sorbent are continuously under attrition process, especially, when fluidization bed is used to perform the reaction. The high velocity of particles is causing increase interaction between particles, what tends to more attrition more likely than in case, where particles are fixed. Also, heating rate in FB reactors is much higher, what additionally favors attrition [64]. On the other hand, the presence of

sulfation reaction in the reactor is making the surface of sorbent harder, what prevents from further attrition [65]. The process is taking place much faster after injection of the material to the bed, what gives both coarse and fine particles.

One of the ways of handling both attrition and sintering of sorbent grains is to use pretreatment methods in order to decrease its influence on sorption capacity and regenerability. The crucial moment for attrition is the first cycle of a sorbent, in every next attrition rate becoming smaller. In terms of sintering, conditions of maintaining process are important, as well as other substances, like water vapour, which are present in the stream. For results of both side effects, specific temperature favors degradation processes, this is why the determination of fitted range is crucial to commercializing process in future and use it to large extent.

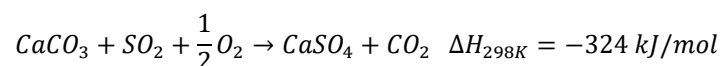
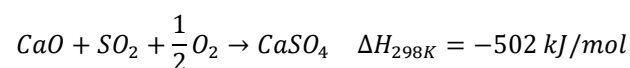
Influence of other compounds present in flue gases

As flue gases consist of various compounds in a different composition, their influence on capture process should be taken into account. One of the most important compound group needed to be taken into consideration are sulphur ones. During gasification process sulphur present in fuel is forming H₂S, while for post-combustion application sulphur oxides are present in the outlet stream. In fact, calcium affinity to bond sulphur compounds is commonly used as a unit for Flue Gas Desulphurization (FGD), where flue gases are reacting, depending on a type of FGD system applied, with limestone or with a colloidal solution of lime, what tends to form calcium – sulphate or sulphite. The compound, which can result from the reaction of calcium with sulphur depends on temperature, according to table presented in [57].

Table 1 Formation of calcium sulphur compounds with respect to conditions

Temperature range °C	Oxidizing conditions	Reducing conditions
<450	CaSO ₃	
<650-700	CaSO ₃ , CaSO ₄	CaSO ₃ , CaSO ₄ , CaS
700+	CaSO ₄	
830+		CaS, CaSO ₄

The problem arises significantly in the case of usage calcium directly in the furnace. Due to the fact, that coal can contain up to 8% of sulphur, following reactions can be observed:



Sorbent, which reacts with sulphur is then deactivated and its capture capacity is no longer available. The reaction is taking place at the surface of the sorbent, CaO is trapped inside of the layer made of CaSO₄, successfully prevents further conversion of that particle. In post-combustion capture prevention of sulphur influence can be done by locating CCS technology after FGD unit. However, this limitation of the can is in fact also an advantage due to the fact, that sulphur captured in such a way is no longer present, what causes the possibility of avoiding installation of FGD in the plant, having sulphate emission at a satisfactory level.

Other important issue regarding usage of calcium as an adsorbent for CO₂ capture is water steam presence in to flue gases. It is essential to take it into account due to high concentration in outlet, which is up to 14%. However, its presence can be treated as both beneficial or limiting agent in case of the reaction between CaO and CO₂. The presence of steam in flue gases leads to faster sinterization of the CaO particles, followed by faster porosity reduction of the material itself, especially in presence of both H₂O and CO₂ in stream as well [58]. All of the effects are dependent on environment factors, temperature and pressure, but also on steam concentration in flue gas stream. Influence of steam on CaO sorbent for CO₂ capture in high temperature was examined in [59]. In this work a several concentration of steam vapour in gas was examined. The interesting behaviour of the examined materials was, that presence of steam improved carrying capacity of the sorbent during cycles. Even better results were obtained, when steam was present during both calcination and carbonation reactions. Concentration of H₂O was making difference for up to 1% in stream, above that level, none of the further improvement was observed. The better results of the steam containing streams potentially can be explained by higher diffusivity during the process. When water vapour is present in carbonation stage, it allows to decrease diffusion resistance through the layer of carbonate, when during calcination, steam is leading to create larger pores because of the sintering, while it is present in both stages it is tending to create bigger pores harder to block and lower diffusion resistance.

One of the suggested results of CaO and ash interaction can be also a undesired component called belite (Ca₂SiO₄), as well as other compounds, however, their presence in the process can be neglected due to very limited amount of Ca taking part in that reactions [57].

Recent improvements of a process/current development of improvements

All of the factors, which influences the reactivity of sorbents, are limiting usage of CaO as a successful media for CO₂ capture. Satisfactory capture of Greenhouse Gas occurs only a couple of first cycles with a fresh sorbent, after several capacities drop significantly, up to 70% after 30 cycles [66]. Because of that, vast of scientists are looking for solutions, which will extend the lifetime of a sorbent, improve its capacity. Currently, we can distinguish between several ways to improve sorbents properties.

Thermal pretreatment

Sorbents which were thermally pretreated were investigated by Manovic et al. [67]. The experiment was made on CaO-based materials on various temperatures and residence time. The temperature was in 800-1300 °C range, while time periods were between 6-48h. After preparation materials were tested in

TGA, carbonation in 50% CO₂ atmosphere and regenerated in pure nitrogen. Resulted materials were exhibited a smaller decrease of sorption capacity during cycles. For sorbents prepared in smaller temperatures (800 and 900 °C) capacities during 30 cycles were continuously decreasing, while in the case of higher temperatures and longer preheating treatment materials were exhibiting effects of self-regenerability and achieved much better results that corresponding sorbent without pretreatment. For the purpose of explaining the effect created, the model of pore skeleton was proposed, presented below [picture from 67, figure 8]. In this representation, two different types of mass transfer were proposed – bulk diffusion observed in CaCO₃ decomposition/formation, and diffusion of ions in CaO crystallites. Crystal structure of oxide is stabilizing the structure, without changes in morphology and carbonations. The whole structure represents skeleton, where hard internal part keeps pores in the same structure, and soft external can be easily changed.

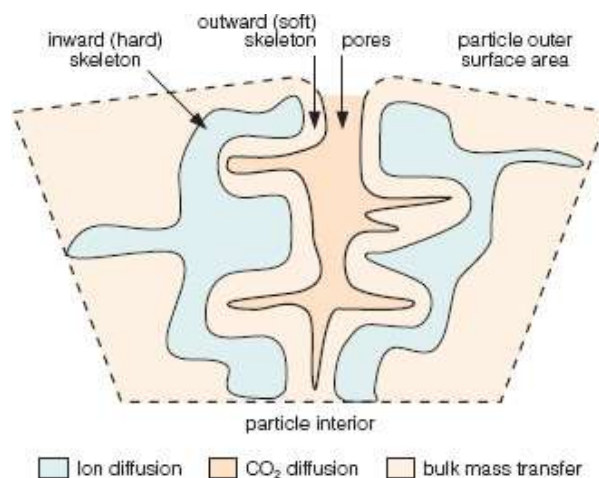


Figure 17 Pore skeleton model [98]

The other interesting observation was made by Chen et al. [68], where the method of pretreatment from [67] was used in 1000 or 1100 °C for 24 hours. After preparation, the sorbent was examined in much longer worktime of 1000 cycles. What was observed, is a fact, that pretreated sorbents had a much bigger affinity for attrition. Apart from that, improvement caused doubled sorption capacity in comparison with the untreated material (15% vs 7.5%). Obviously, a way of thermal pretreatment will mainly depend on an input material, because of the impurities present in sorbent and structural differences, which can have different optimal pretreatment conditions comparing to materials examined in mentioned papers.

Sorbent reactivation by hydration means

Currently, hydration of a calcium sorbents is successfully applied in FGD systems, where it helps to increase the efficiency of a process up to 40% [69]. Following that fact, hydration might be a promising method to reactivate sorbent spent for CO₂ capture. For CCS purpose, regeneration of sorbent should be done in a different manner than in the case of SO₂ sorbents. The best way to perform it is to introduce H₂O in a calcined state in order to avoid limiting factor of carbonate layer, what limits reaction to really slow rates.

Two methods of hydration were examined by Han et al [70], where steam and liquid hydration was taken into account. In the case of liquid hydration, it was performed by distilled water in a shaker at atmospheric conditions after one use, while steam one was performed at 300 °C in the steam-nitrogen atmosphere under 2 MPa pressure after every cycle. In the case of both methods had a beneficial impact on sorption capacity of a sorbent, especially in the case of steam reactivated sorbent, which exhibited a slower decrease of efficiency than liquid hydrated one. The resulting sorbents had increased surface area and porosity, which favored CO₂ diffusion through carbonate layer. Also, the conclusion was, that hydration after each cycle could permanent improve surface development and sorption capacity, however, the method will increase energy penalty caused by the usage of that method. In fact, these results stay in accordance with Manovic and Anthony work [71], who obtained almost doubled carbonation degree after steam reactivation in 200 °C (70% vs 35-50% in original one).

An important factor during hydration of sorbent are obviously conditions of the process itself. Rong et al [72] were examining the frequency of hydration as well as the temperature, with a comparison to sorbent without any treatment. In temperature range between 200-500 °C, it was found out, that the most appropriate temperature of steam hydration is 300 °C, giving the best results during next cycles and material also was improving its sorption abilities after 9 cycles. On the other hand, hydration should occur in a stream containing as much of steam as it is possible – the bigger steam usage was, the biggest uptakes were obtained. What stays consistent, hydration should be performed after every cycle, this technique helped to achieve the biggest conversion with respect to samples hydrated every 3 cycles or just at the beginning of the process.

Hydration has good prospects to overcome problems devoted to sorbent regenerability, however, the necessity of adding another reactor for sorbent hydration results in an additional operation, which has to be integrated into a system. Further investigations should be taken into account, especially including feasibility and profitability of such undertaking.

Sorbent modification

One of the most important methods to improve sorption capacity of CaO sorbent is a modification of material using chemical reagents. Usage of this method can be justified by a fact, that Gupta et al. [73] found out, that natural limestone derived CaO had higher reactivity than from precipitated calcium carbonate. Modification of sorbent mainly bases on increase basic sites on a surface of grains, what extends reaction surface for CaO and additionally prevents from the negative effect of sintering. Currently, vast of materials were examined in order to find the most appropriate one concerning CaO sorbent for CO₂ capture.

Li et al [74] object of interest was a modification of CaO derived from limestone by ethanol/water solutions, with 50, 70 and 90% of C₂H₅OH, dried and investigated during cycles. The resulting sorbent was then investigated during 15 cycles, the higher concentration of C₂H₅OH, the higher sorption capacities were obtained. Another change of sorbent which was observed corresponds to the morphological structure of resulted grains. Median particle size in the case of ethanol treated CaO was smaller, and pores of material were expanded. The results differed more after several cycles, at the

beginning all of the samples were exhibited almost the same sorption capacity. Mixing with formic acid was proposed by Ridha et al. [76]. Resulted pore volume and the low surface area, in this case, were not higher as in the case of untreated limestone, however, modification by 10% of formic acid solution allowed to increase the amount of CO₂ captured by 67.4% after 20 cycles, what is suspected by increased sintering resistance. Formic acid was also used by Li et al, which was trying to modify in a similar manner with pyroligneous acid consisted of formic and acetic acid [77], this modification resulted in carbonation conversion of 33% instead of 7.8% for untreated after 100 cycles. The same authors also performed attempts with acetic acid, which showed slight improvement, especially, when samples were calcined at lower temperatures [78]. Another approach on improving uptakes was proposed by Santos et al., who were using a sol-gel method using equimolar amounts of citric acid monohydrate and calcium nitrate tetrahydrate [80]. Resulted sorbent was characterized by high surface area and reasonable sorption capacity after 18 cycles, however, after 70 cycles dropped to 0,24g of CO₂ sorbed per gram of CaO.

One of the other groups of compounds used for enhancement of CaO sorbents were a different type of salts. Salvador et al. performed experiments on NaCl and Na₂CO₃ influence on the reactivity of material [79]. Unfortunately, this method caused completely reverse effect – reactivation of sorbent treated by Na₂CO₃ and NaCl was much less efficient than in the case of limestone without modification, as well as reduction of CO₂ sorption capacity. On the other hand, Reddy and Smirniotis [81] were examining chlorides of metals, which belonged to the 1st group. Metals were chosen because of their basic nature, which favors chemisorption of CO₂. Examined sorbents were prepared by means of wet impregnation method using analytical grade calcium oxide and corresponding chloride of alkali metal. The result of the investigation was a correlation between electropositivity and improvement – the bigger electropositivity, the better dopant, especially when it comes to cesium. Wet impregnation was also used by Sun et al. in the investigation of manganese salts influence on sorption [82]. The materials used were analytically pure MnCO₃ and Mn(NO₃)₂. Resulted material at an initial number of cycles had a smaller capacity than original CaO, however, a decrease of activity was smaller in time, what allowed to achieve bigger capacity in 100 cycles by 69%. This result was explained by the better abundance of pores with Mn-doped material relative to original one.

Materials, which were also examined in order to enhance properties of CaO sorbents desired for CO₂ capture were metal oxides. Koirala et al. prepared their sorbents by means of flame spray pyrolysis (PSP) and doped CaO on calcium zirconium oxide [83]. This compound was chosen as a stabilizer because of its Tammann temperature and refractory nature. Sorbents with incorporated Zr allowed to achieve molar conversions of 45% after 100 cycles. High specific surface area, together with large pore volume allowed to remain excellent sorbent properties even under high temperatures of decarbonation, performed at 900 °C. Zirconium oxide was also examined by Broda and Muller [85]. In their work sol-gel method was used in order to dope CaO on ZrO₂. Used precursors for that purpose were calcium nitrate, hydroxide and acetate. The result of investigations were materials with high surface area and pore volume, as well as favourable CO₂ capture characteristics. Comparing to limestone used as a reference, uptake on Other proposed material is aluminium composite metal oxide described by Li et al. [84]. Formed material Ca₁₂Al₁₄O₃₃, combined with CaO by mixing aluminium nitrate enneahydrate with CaO

in mixture of 2-propanol and water, was in ratio with CaO/ Ca₁₂Al₁₄O₃₃ 75/25 (wt%). Obtained material was able to achieve 41% of CO₂ sorption capacity after 50 cycles, what is remarkable value in mild conditions, the more severe conditions, the less uptake was observed, decreased to 22 wt%.

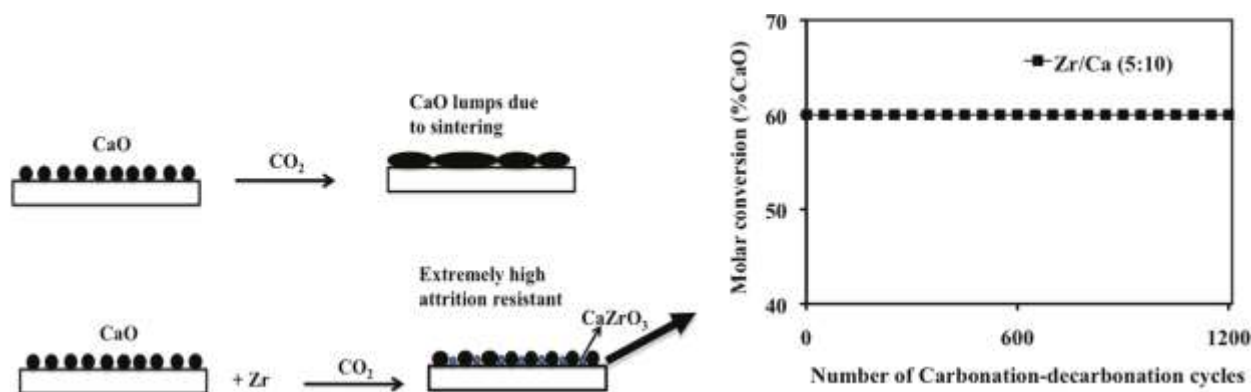


Figure 18 CaO doped on zirconia approach [83]

Manovic and Anthony in their work proposed usage of stabilizer such as bentonites or cements for a sorbent, which is also hydrated, in order to bind very fragile particles which are result of CaO treatment with hydration [77]. The goal of the experiment was to obtain pellets stabilized for capturing CO₂, which should be sintering and attrition resistant. Unfortunately, the results have shown, that bentonites are not suitable for such an application, they are causing more extensive sintering and formation of new compounds locally, such as Ca₂(SiO₄) or Ca₅(SiO₄)₂CO₃, while cements are promising materials which are not favouring any degradation of a material. Qin et al on the other hand proposed preparation of CaO sorbent by means of wet mixing with materials considered as wastes [75]. Analytic grade CaCO₃, Ca(OH)₂, calcium acetate hydrate, D-gluconate, formate and L-lactate were mixed in ratio 75/25 or 50/50 with supports as cement, clay and fly ash in water, then dried and calcined. The biggest uptake and deactivation resistance was observed with a samples made of organometallic precursors and cement. Authors indicated, that steam presence would improve the results. Also it was found out, that organometallic precursors usage resulted in excellent pore structure in the beginning and inert materials used were able to sustain basic framework of the sorbents. However, the problem indicated with resulted material was attrition, which impact should be decreased in further development. Also, authors noticed a problem of costs, caused by using organometallic precursors instead of mineral derived raw material.

Feedstock for Calcium Looping Cycle sorbent preparation

All of the CCS technologies considered to use as an efficient option for CO₂ removal needs to fill one necessary condition – the raw material for processing should be cheap, abundant and easy to dispose of considering waste generated during cycles. One of the biggest advantage of calcium as a sorbent for CO₂ capture is extremely cheap and occurs in the vast amount of forms in the environment.

Apart from analytical grade reagents used for applicability of Ca material investigations, the most used raw material for sorbent preparation is limestone – sedimentary rock, which deposits can be found all over the world [60]. Limestone nowadays is important construction material, mainly composed of CaCO₃, there occur rocks with chemical grades up to 95% of CaCO₃ [86]. Thanks to its chemical composition, limestone is a material which allows obtaining almost pure CaO used for sorption.

However, it is not the only material investigated as a potential feedstock. Chen et al. in their work compared two most common rocks when comparing their abundance, so limestone and dolomite [87]. Dolomite is mainly composed of both calcium and magnesium oxide. It was found out, that dolomite lost less of its sorption capacity in time comparing to limestone, and even better results were obtained, when raw material was thermally pretreated; after 50 cycles non-treated dolomite had efficiency at the level of 0,4 utilization efficiency, while limestone 0,11. On the other hand, Aguilar proposed other material which is also derived from rocks, and it is waste marble powder [88].

Other materials, which can be taken into account considering calcium source for CO₂ capture are biogenesis wastes. Witton proposed obtaining sorbent-derived from eggshells [89]. This material is composed mainly of calcium carbonate, after calcination of eggshells concentration of CaO in tested eggshells was at the level of 97.42% of the total sample. In that work, uptake of eggshells derived material was significantly bigger at the beginning of 11 cycle performance, as well as at the 11th cycle, where difference in uptake was equal to 20%. Difference between two materials was explained by smaller CaO particle size, what resulted in higher surface area for the reaction. More extensive study was performed by Castilho et al., who examined nine different wastes from food, including variety of shells, crab cuticles and eggshells as well [90]. All of the materials were investigated in terms of surface area and pore structure, as well as chemical composition before and after calcination of all of the materials. After that, cycles of 10 carbonation/decarbonation were performed. Resulted calcined material was characterised by small porosity, confirmed by BET analysis, followed by small particle diameters. Considering capacities of investigated materials it could be found, that eggshells and scallop shells presented bigger capacities and better resistivity to decrease their uptake. Also materials differed in change of the uptake in time, eggshells, scallops were continuously uptaking bigger amounts of CO₂, while materials like cockles, cuttlefish bones and snail shells were instantly achieving its maximum and after rapid uptake in slower stage the uptake was nearly close to constant. This behaviour of examined material can be justified by different chemical composition, which influences kinetics of uptake.

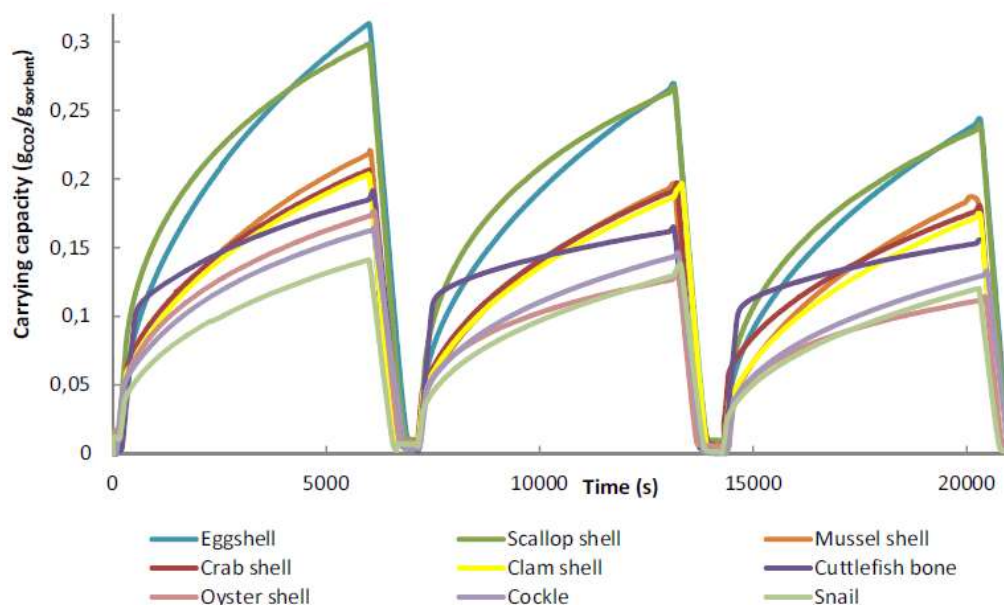


Figure 19 Comparison between various type of bioderived CaO sorbents

3. Materials and methods

Raw materials

In present work main raw material used for sorbent preparation was the eggshell powder. It was prepared from eggshells collected from households, which were rinsed and then dried in order to remove remaining organics inside. After collection of material, all collected were crushed and then grinded in agate mortar.

Sorbents before examination of its usage were modified using analytical grade reagents with certain amounts of chemicals in a strict way. Generally, we can distinguish between four groups of sorbents used: dry mixed eggshells with metal carbonate salts, dry mixed eggshells with silicon oxide and sol-gel like treated eggshells with zirconia and silicon oxides. Additionally, calcined eggshells were prepared as a reference material. In the case of sol-gel like treated sorbents procedure included the addition of lactic acid. All of the chemicals used in sorbent preparation are presented in the table below:

Table 2 List of used reagents

Name	Molecular formula	Manufacturer	Purity	Molecular weight
Silicon dioxide	SiO ₂	Evonik		60.08
Strontium Carbonate	SrCO ₃	Aldrich	98	147.63
Sodium Carbonate 10-hydrate	NaCO ₃ 10 H ₂ O	Panreac	99	286.14
Lithium Carbonate	Li ₂ CO ₃	Allied Chemical	99	73.89
Manganese Carbonate	MnCO ₃	Riedel-de Haen		114.94
Cerium (III) nitrate hexahydrate	Ce(NO ₃) ₃ 6 H ₂ O	Acros Organics		434.22
Magnesium carbonate	MgCO ₃	Mallinckrodt	99	144.32
potassium carbonate	K ₂ CO ₃	Merck	99	138.21
Titanium (IV) oxide	TiO ₂	Aldrich	99.7	79.9
zirconium (IV) oxide	ZrO ₂	Aldrich	99	123.22
2-hydroxypropanoic acid (Lactic acid)	C ₂ H ₄ OHCOOH	Aldrich		

Sorbent preparation

Materials used were prepared by three different methods. The first sample used as a reference for modification results was calcined, previously ground and crushed eggshells.

The first method which was used for sorbent preparation was dry mixing. In this method, eggshells were introduced to mortar together with a modifier and then ground again. This operation allowed obtaining uniform mixing of both materials together with the formation of sorbents' satisfactory particle size distribution. After grinding-mixing materials were calcined at 900 °C during 4 hours.

The second group of sorbents made was sorbents treated by lactic acid and modifier, which in thesis is called sol-gel like method. The method itself is In this case, both eggshells and modifier were introduced to demineralised water. This mixture was agitated on a magnetic stirrer in order to obtain a suspension of insoluble materials. Beaker content was heated up to a temperature of 70 °C and lactic acid was introduced into small parts, in order to prevent overflow from the beaker. Added lactic acid was always 10% of introduced solids total mass, and the mixture was maintained in that condition for 30 minutes. After that, the mixture was heated above the boiling point in order to evaporate water present in suspension and after that calcined.

Since sintering is strongly temperature dependent, one of the crucial parameter, when investigating chemisorption of CO₂ is Tammann temperature. This value gives a sense of atoms mobility. It must be conceded, that as the temperature is closer to the melting point, compound molecules are moving more likely, what may lead to increase of sintering of particles[100]. Obviously, this value is not a crucial and sintering rate determining factor, however, it can be used to predict some behaviors during long run cycles. All of the melting temperature, together with corresponding Tammann temperatures in °C are presented in Table 3.

*Table 3 Melting and Tammann temperatures gathered, when compound is noted with *, it means, that initial modifier was carbonate, which decomposed during calcination as a preparation step, ** stands for quartz*

Compound	T _{melting} [°C]	T _{Tammann} [°C]
CaO	2572	1149,5
ZrO ₂	2715	1221
SiO ₂ **	1600	663,5
K ₂ CO ₃	891	309
Li ₂ O*	1438	582,5
MnO*	535	131
Na ₂ O*	1132	429,5
SrCO ₃	1494	610,5
MgO*	2852	1289,5

As can be noticed, some of the modifiers used, like ZrO₂ and MgO are having really big Tammann temperatures, so it can be concluded, that this particular samples will sinter less likely, on the other hand, metal oxides, such as MnO, Na₂O, together with K₂CO₃, are exhibiting very low Tammann temperature, what may lead to increased rate of surface degradation. Very interesting from the point of view of the process will be a modification, which Tammann temperatures lie slightly below the

temperature range, which is used for carbonation-decarbonation longrun cycles. It can be interesting, how the mobility of this modifier will influence the performance of the sorbents.

Techniques of sorbent characterization

X-ray diffraction (XRD)

XRD is a technique which uses X-ray diffraction for identifying, quantifying and characterising of examined sample. Examined material is sampled with a monochromatic beam of X-ray photons. Information about crystal planes occurrence is provided by a scattering angle of X-rays which were diffracted by the lattice. Reflected X-ray intensity is presented as a function of doubled angle of diffraction, a method is based on diffraction of an X-ray radiation from crystalline sites. Radiation is deflected from a surface of the examined material at certain angle theta. The relation between diffraction angle 2θ and spacing of materials' lattice is described by means of a Bragg's law.

XRD allows distinguishing between solid material crystalline phases taking into account XRD patterns of materials with the distinctive fingerprint of different crystalline material. Also, XRD can be used for determination of crystal sizes. This can be done by application of the Scherrer equation. This operation, as well as comparison with patterns, were done using special software delivered by the equipment manufacturer.

Non-destructive of a material is a major advantage of using XRD, especially when examined materials are in really small amounts. The main limitation of that technique is its usage only for crystalline materials, XRD is not detecting small amounts of amorphous materials. For the purpose of examining materials used for experiments, Bruker D8 advanced X-ray diffractometer, equipped with a copper tube, graphite monochromator and scintillation counter. Diffractograms were created using Cu- α radiation at 40 kV and 40mA in 3-70° range.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) is used for examination of changes in mass of an examined sample in respect to temperature and time, in present of certain gaseous media. Usage of TGA is very wide – it can be used for investigation of chemical decomposition, devolatilization, but also for observation of chemisorptions and solid-gas reactions. Typical TGA apparatus consist of precision balance, at which pan with the sample is placed, programmable furnace and thermocouple for temperature control.

The other data which may be obtained using TGA are Difference Thermogravimetric ones (DTG). This one is giving a sense of how fast the change of examined sample in respect to temperature and time. The technique is useful, when one wants to examine samples and determine temperature of forming and decomposition of specific compound.

From the point of view of investigations performed in this work, two types of operations were performed using TGA analyser. First one was a change of mass of treated sample in respect to temperature, what allowed to examine materials in terms of initial sorption capacity and choose preliminary materials which should be examined in the long run experiment. The heating rate of all runs was the same. Long-term

experiments were ten of carbonation-calcination cycles at comparable conditions for each of samples. Conditions for both types of runs on TGA are presented in tables below:

TGA analysis was performed on Netzsch STA 409 PC thermobalance connected with a flow controller connected with sources of CO₂ and N₂ used to create reaction environment. The system was also connected to a thermostat in order to improve cooling rate of samples.

Specific surface area and pore volume

Brunauer, Emmett and Teller theory is explaining adsorption of gas molecules on a solid surface. BET method is a practical application of the mentioned theory. Porous solid sample adsorption is examined by the interaction between the material and inert gas. Because of the usage of inert gas, the surface has to be cooled down sufficiently in order to observe any adsorption on a surface. The amount of gas adsorbed is corresponding to the surface area of the particle, taking into account also the pressure of a gas, temperature, and interactions between solids and gas in that particular system.

Barrett Joyner Halenda (BJH) analysis was used in order to determine pore volumes. The method uses modified Kelvin equation to relate amount of adsorbate present in pores as the relative pressure is decreased.

Scanning Electron Microscopy SEM-EDS

SEM allows examination of a particle when it comes to morphological structure. A beam of electrons with narrow energy distribution focuses on examined sample surface. The sample itself is kept in high vacuum in order to avoid movement of electrons. What is measured in SEM technique are yields of electrons interacted with atoms of a sample and beam position with the detected signal are producing the image of surfaces presented on a material. SEM produced signals are secondary electrons, reflected or back-scattered electrons, photons of X-rays and light, absorbed current and transmitted electrons.

SEM analysis was performed on Hitachi S-2400 microscope, with working distance 5mm and accelerating voltage of 20kV. The samples before examination were coated by the Au-Pt thin film to allow observations.

4. Results and discussion

Specific surface area and pores characteristics

Specific surface area, both with pore volume and average pore size are a helpful indicator to assume their applicability for CO₂ capture. Increased specific surface area, together with bigger pore volume will contribute to higher and faster CO₂ uptake at initial stages of carbonation-decarbonation cycles, allowing to sustain the process in kinetic stage instead of diffusional one. Results of the surface analysis are presented in Table 4.

Table 4 Results of surface analysis for each sorbent

Modification applied	S _{BET} [m ² /g]	Pore volume (BJH) [mm ³ /g]	Average pore size (BJH adsorption) [nm]	Average pore size (BJH desorption) [nm]
Unmodified Eggshells	7,3	7,8	3,94	4,88
ZrO ₂ 5%	9,8	13,8	4,56	5,05
SiO ₂ 5% sol-gel-like	12,4	15,3	4,13	4,68
SiO ₂ 5% dry mixed	4,5	7,9	4,68	5,52
Na ₂ CO ₃ 5%	11,7	23,6	4,83	6,13
5% MgCO ₃	13,1	24,6	4,59	5,81
5% MnCO ₃	9,1	17,4	4,53	5,82
5% K ₂ CO ₃	8,3	9,4	4,02	4,75
5% SrCO ₃	8,1	11,6	4,11	5,02
5% Li ₂ CO ₃	9,0	19,0	5,25	6,78

According to the results, only one of the proposed modification has not improved its specific surface area together with pore volume (value lies in the range of error). This fact can be a significant sign, that in the case of every modification except dry mixed SiO₂ have improved sorption performance, what might be observed during longrun tests. However, the shallowness of pores, indicated by their volume may lead to the conclusion, that during process CO₂ uptake will be decreasing constantly due to attrition of particles throughout cycles. Average pore size presented and compared with IUPAC classification are in fact evidence, that during sorbent preparation we are dealing with mesopores[101]. What might be a good information, when taking into account pore blockage, however, it is certain, that voidages on particles, sooner or later, will be subjected to sinterization, which will block calcium oxide present inside pores and lead to sorbent deactivation.

What can be noticed is an excellent specific surface area both with pore volume when taking into account samples modified with Na₂CO₃ and MgCO₃. This might be a result of monophasic spacer effect, which successfully increased distances between CaO molecules, eventually leading to significant specific

surface area improvement, however, in the case of Na_2CO_3 , good sorption capacities are not suspected due to its low Tammann temperature value.

What can be also noticed, is a beneficial effect of sol-gel like method on surface improvement. Samples treated by means of this method have shown significant improvement of an area (except sorbents mentioned in the paragraph above), what is especially visible when comparing two samples with SiO_2 as a modifier. It can be said, that usage of lactic acid as a chelating agent improved surface development, indicating decomposition of lactic acid as a possible cause.

XRD Diffractograms of examined samples

XRD technique allows characterizing the samples chemical composition. It can be done by comparing resulting diffractograms with patterns of compounds, which presence in a sample is suspected. Information, which can be obtained from these data, is essential when taking into account completeness of calcination and further changes of a sorbent during adsorption tests. All of the samples were compared to lime standard, which is the most important compound for CO_2 sorption, but also with portlandite, the mineral form of calcium hydroxide and calcite, which was the raw material for sorbent preparation. Additionally, diffractograms of samples modified with ZrO_2 were additionally compared to ZrO_2 standard, as well as SiO_2 modified with the SiO_2 pattern. Diffractograms, as well as standard peaks locations, are collected on graphs below.

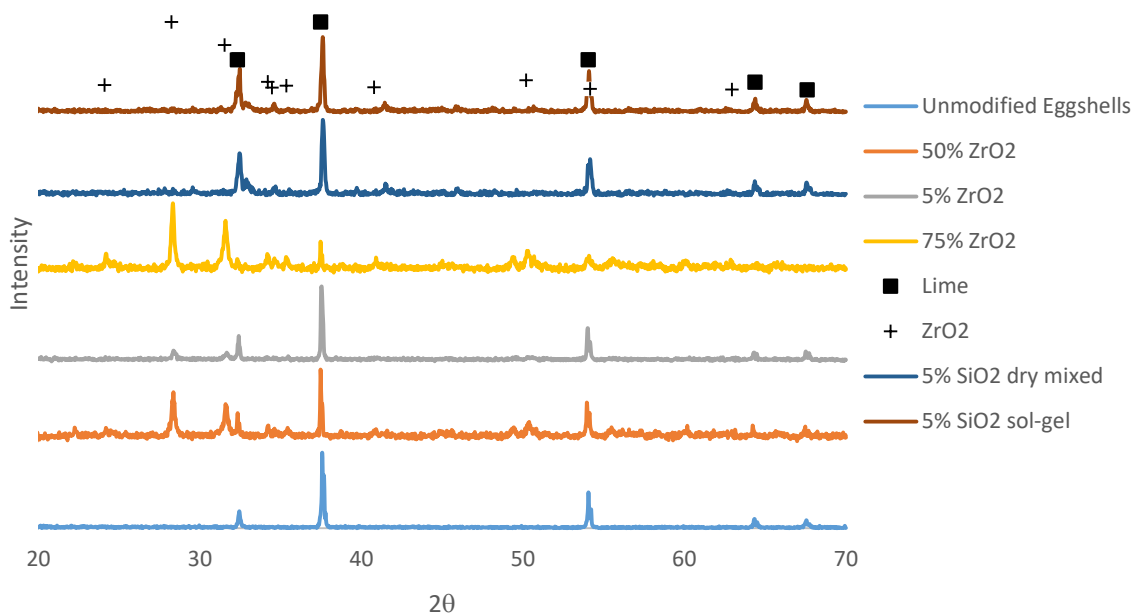


Figure 20 XRD diffractograms of samples prepared with ZrO_2 and SiO_2

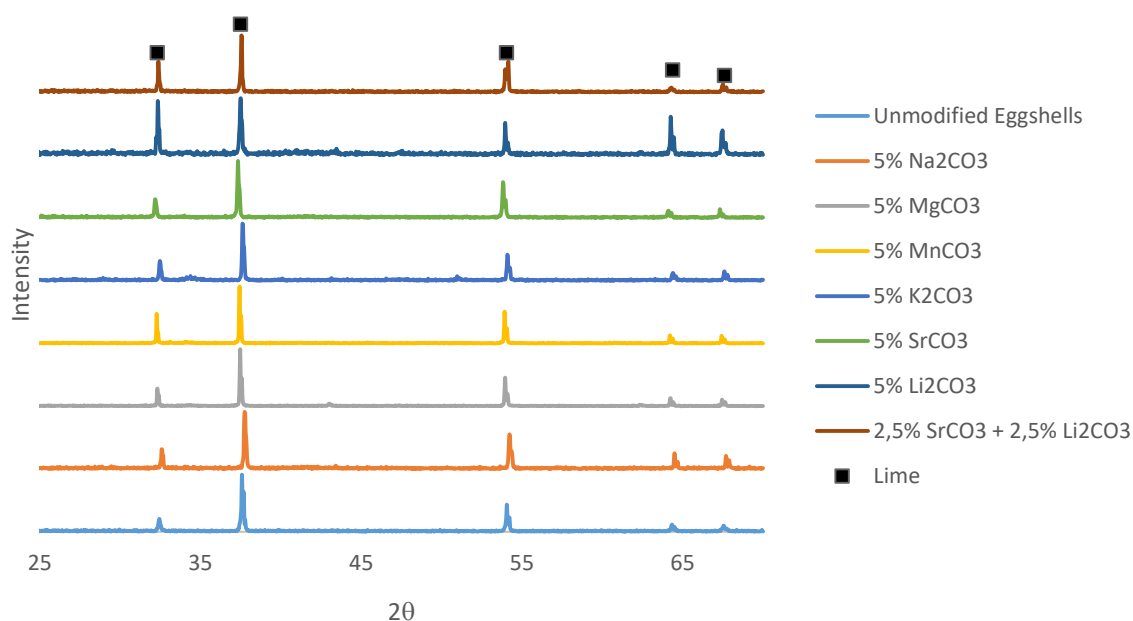


Figure 21 XRD diffractograms of sorbent prepared with carbonate salts

As it can be seen in the case of almost every case, the main constituent of prepared sorbent is lime itself. Long-time of calcination used for sorbent preparation was sufficient to successfully decompose calcium carbonate, from which eggshells are composed of. In terms of all carbonate salts modifiers, their influence on the chemical composition of a sorbent was minor and have not presented any significant changes of diffractograms. In some cases, there are peaks observed, which does not belong to lime, but to calcium hydroxide. Its presence can be justified by the presence of water adsorbed during sample preparation. Similarities in all of the diffractograms before sorptions are in fact the evidence, that CaO, except adsorption of H₂O molecules, does not interact chemically with modifiers, leaving CaO in the same form as before sorbent preparation. It is important from calcium utilization point of view since the total amount remains in oxide form and may react with CO₂ itself.

The samples, in which difference between diffractograms are the biggest, are the ones modified with ZrO₂ and SiO₂. It is the effect of the ZrO₂ amount in sorbent, which can be observed when comparing to the ZrO₂ pattern. Increasing amount of zirconia used causes increasing peaks connected with this compound. Zirconium oxide, as an unreactive material, has not formed any other compound with calcium, as well as have not decomposed in high temperature, creating a support for eggshells' promoted sorbent. By increasing amount of modifier, a corresponding increase of ZrO₂ peaks is observed. As it comes to sorbents modified with SiO₂, there exist peaks, which can represent both silicon oxide, which in fact was the modifier itself.

Morphology of examined samples

Fresh samples morphology was determined by means of scanning electron microscopy. The technique used allowed to carefully examine sorbents in terms of initial shape and size of particles formed after initial calcination of material.

As for calcined unmodified material, it can be seen, that calcined eggshells formed diverse particles, which vary in shape and size. What can be noticed is a fact, that bigger particles consist of smaller ones agglomerated into one bigger. CaO, which is the main constituent part, forms agglomerates with reasonably big voidages between smaller parts of particles. It is suspected, that during carbonation of these samples empty spaces are covered by freshly formed CaCO₃, what can significantly inhibit the process and decrease sorption capacity of examined sample up to the moment, in which particles will be completely sintered and it will be impossible for CO₂ stream to react with inner CaO due to diffusivity limitations.

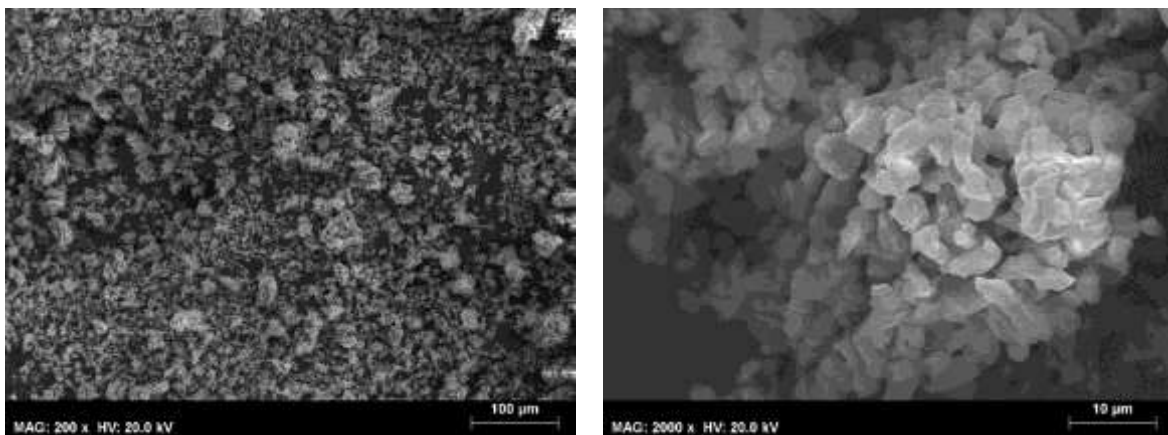


Figure 22 SEM images of calcined eggshells

As for samples prepared by dry mixing, significant diversity in terms of morphology can be observed. Poor development of surface can be noticed on Na₂CO₃ particles. Moderate size agglomerates are tending to form rounded shape particles, however, no significant pores can be observed, what possibly can decrease sorption capacity of the sorbent.

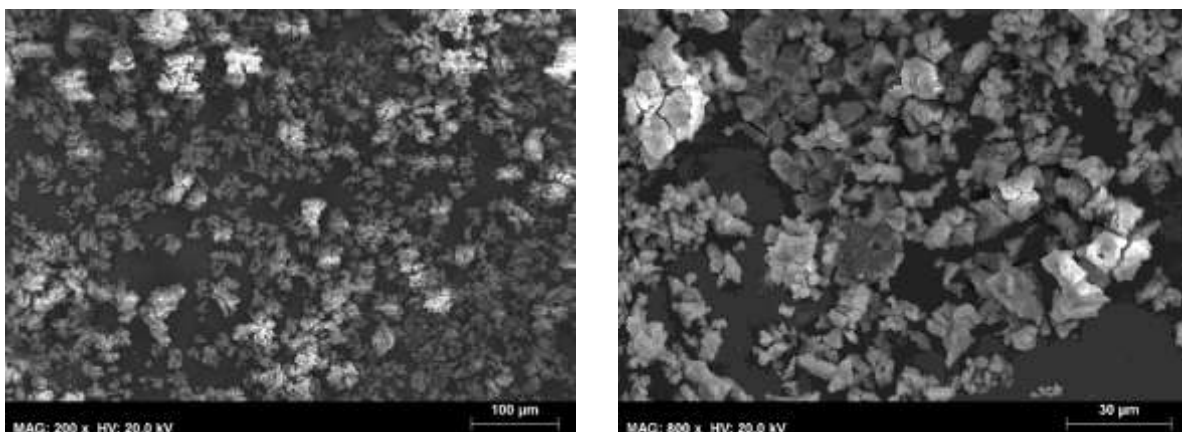


Figure 23 SEM images of fresh Na₂CO₃ modified samples

Very similar effect can be observed on modification with K_2CO_3 . In this case, big voidages can be observed, what, to a small extent, can affect sorption capacity by improving it slightly.

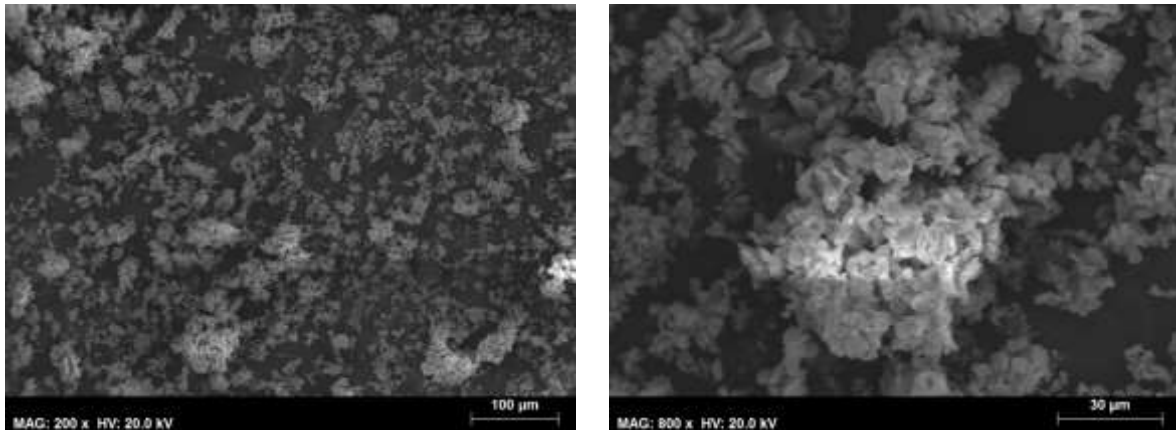


Figure 24 SEM images of fresh K_2CO_3 modified samples

When it comes to sample modified with 5% $MgCO_3$, particles are significantly smaller when comparing with previous modification, however, there exist some long particles, which origin is from MgO , formed by calcination of $MgCO_3$. Poor mixing of the sample with modifier can be one of a possible explanation of poor sorbent performance. If this will be applicable, since modifier itself had not modified eggshells particles, rather remained untouched.

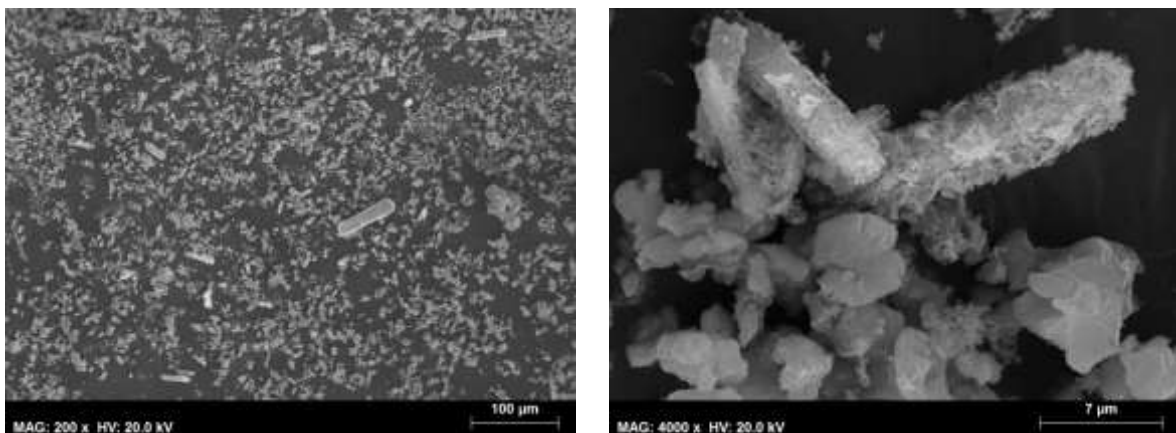


Figure 25 SEM images of fresh $MgCO_3$ modified samples

Very complex shape of particles can be observed when taking into account $MnCO_3$, however, it can be considered as a shallow one, what may lead to the dramatic effect of attrition on this samples.

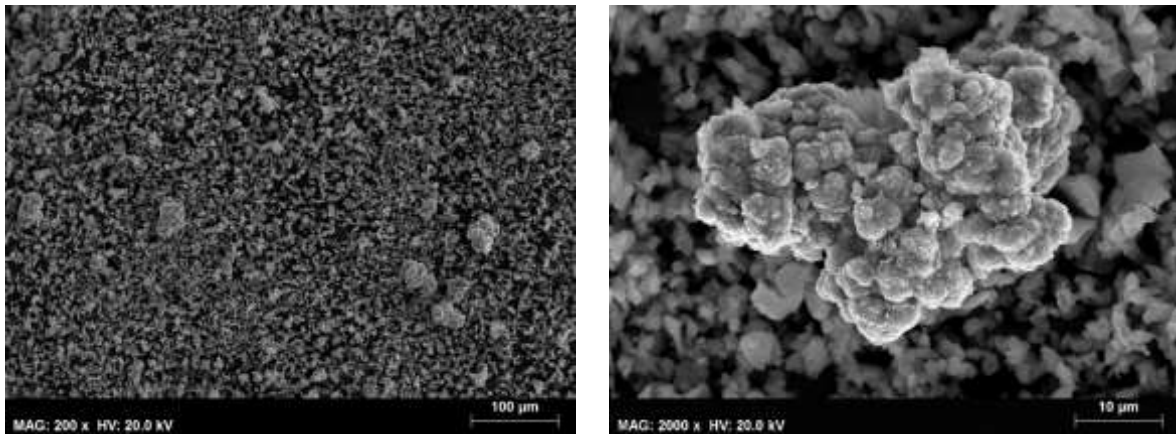


Figure 26 SEM images of fresh $MnCO_3$ modified sorbents

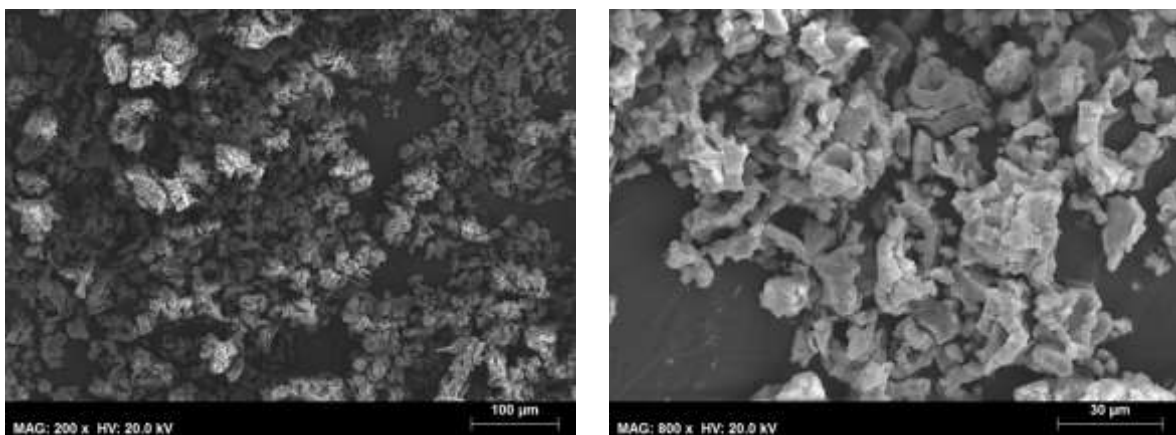


Figure 27 SEM images of fresh Li_2CO_3 modified sorbent

Significantly better morphology in terms of CO_2 capture applicability is observed when $SrCO_3$ and Li_2CO_3 are taken into account. In this two samples well surface development can be observed, as well as big porosity and small particle size. This can be especially noticed, when taking into account $SrCO_3$, where even if the agglomerates are bigger, their structure is very complex, with a multitude of shape variation. When looking at Li_2CO_3 SEM images, a large amount of pores with big volume can be observed. This may possibly be beneficial for the carbonation process at first stages. After several cycles there exist a possibility, that pores will be blocked, what will promote diffusional stage of carbonation instead of kinetic one, when CO_2 will need to permeate through newly formed carbonate, what on the other hand will decrease capture rate.

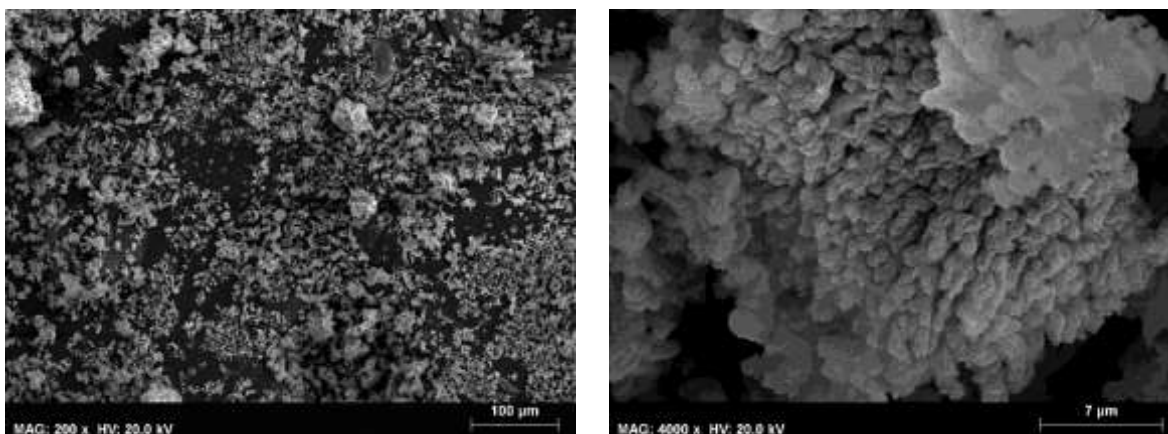


Figure 28 SEM images of fresh SrCO₃ modified sorbent

The last sample prepared by means of dry mixing was SiO₂ modified sorbent. particles of this modification exhibited strong affinity to form large agglomerates. When taking a look on the surface, it is clear, that this sample has suffered sintering during calcination. Poor surface development, together with big agglomerates are the evidence of this fact. Moreover, when taking a look at the surface of agglomerates, no voids can be observed, and sinterization is on very advanced stage, what can be observed, looking on the way, how dense particles are packed. It is suspected, that among all of the sorbents prepared by means of dry mixing, this one would have the worst performance.

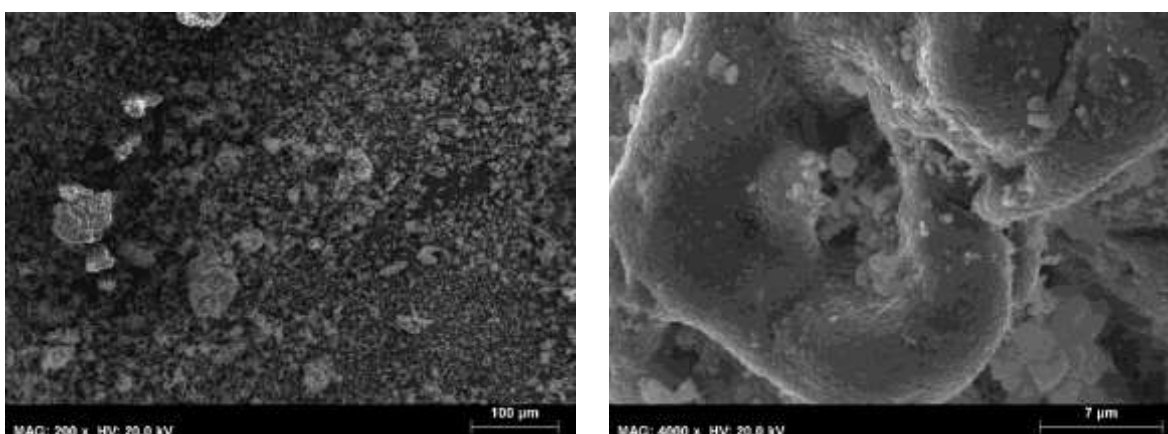


Figure 29 SEM images of fresh SiO₂ dry mixed modified sorbent

Taking a look at samples prepared by sol-gel like method, significantly bigger development of surface can be observed, especially, when comparing SiO₂ prepared sorbent by dry mixing and with the usage of lactic acid. Significantly more complex surface, with small particles attached and increased porosity, may lead to the assumption, that these sorbents will exhibit significantly bigger ability to uptake bigger amounts of CO₂. Also noticeable is a big diversity of particle size and their agglomerates. Both in the case of ZrO₂ and SiO₂, this structure may be caused by the formation of calcium lactate, which during calcination decomposed and formed these sophisticated structures.

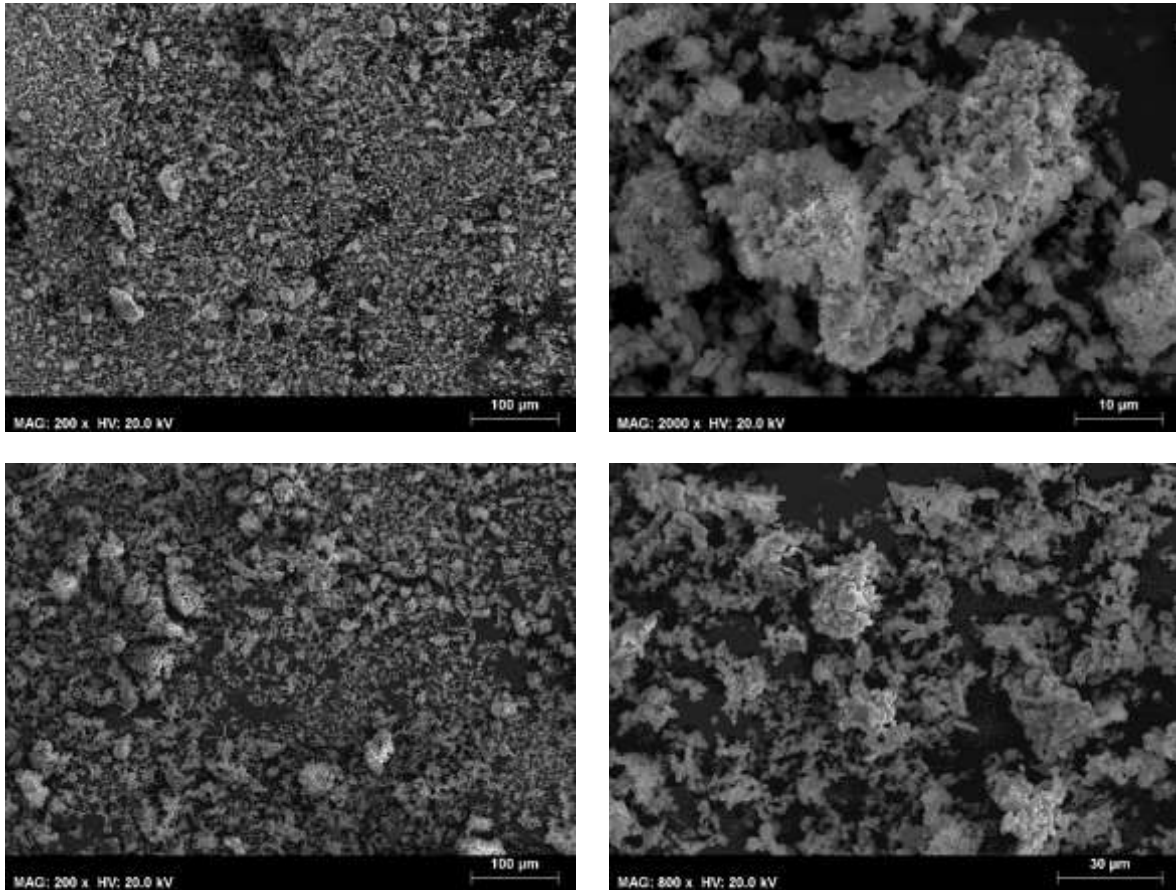


Figure 30 SEM image of fresh SiO₂ modified sorbent prepared by sol-gel like method (upper part) and fresh ZrO₂ modified sorbent prepared by sol-gel like method (lower part)

Dynamic investigation by TGA

The primary test for all of the samples investigated in the thesis was dynamic sorption in constant temperature change. This allows to determine “most promising” sorbents when it comes to initial sorption capacity, as well as choosing appropriate temperature for long run tests. Samples were introduced to pan inside TGA, then heated with constant rate across the whole temperature range. The conditions, in which dynamic tests were made are presented in the table below:

Table 5 Dynamic sorption tests conditions

Initial temperature	20 °C
Final temperature	1100 °C
Heating ratio	20 °C/min
Gas composition	20% CO ₂ (V/V)
	80% N ₂ (V/V)

Evaluation of dynamic sorption for each of sorbent allows also to determine temperatures, in which process will be performed in the most suitable regime, as well as temperature for decarbonation of samples in multi-cycle tests.

As for the dynamic sorption graphs, we can distinguish several phases, which changes when the temperature is rising. The increase of the sample mass in the region of 550 °C, which appeared in the case of some samples, is a result of carbonation of a modifier. It is visible especially in the case of carbonate salts used for modifications, particularly lithium, sodium and magnesium carbonates. The second phase is a kinetic sorption of CO₂ from gas. It can be characterised by the high rate of sorbent's mass increase. The next is a diffusional stage when kinetic stage ends and CO₂ is passing through particle by diffusion. This one is highly dependent on the diffusivity of examined material, as well as significantly slower than the kinetic stage, which occurs on the surface. The last stage is decarbonation, when carbon dioxide is detached from sorbent and calcium oxide is then recovered. All of the samples were compared to raw material, which was unmodified calcined eggshell powder. Resulted thermograms are presented on the picture below.

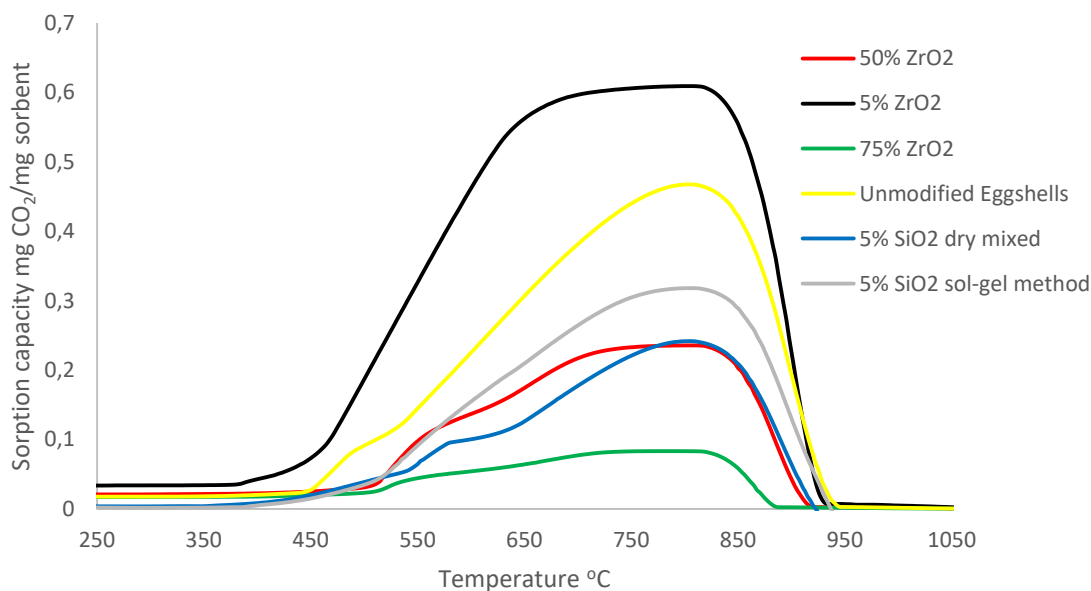


Figure 31 Thermograms of ZrO₂ and SiO₂ modified sorbents during dynamic test

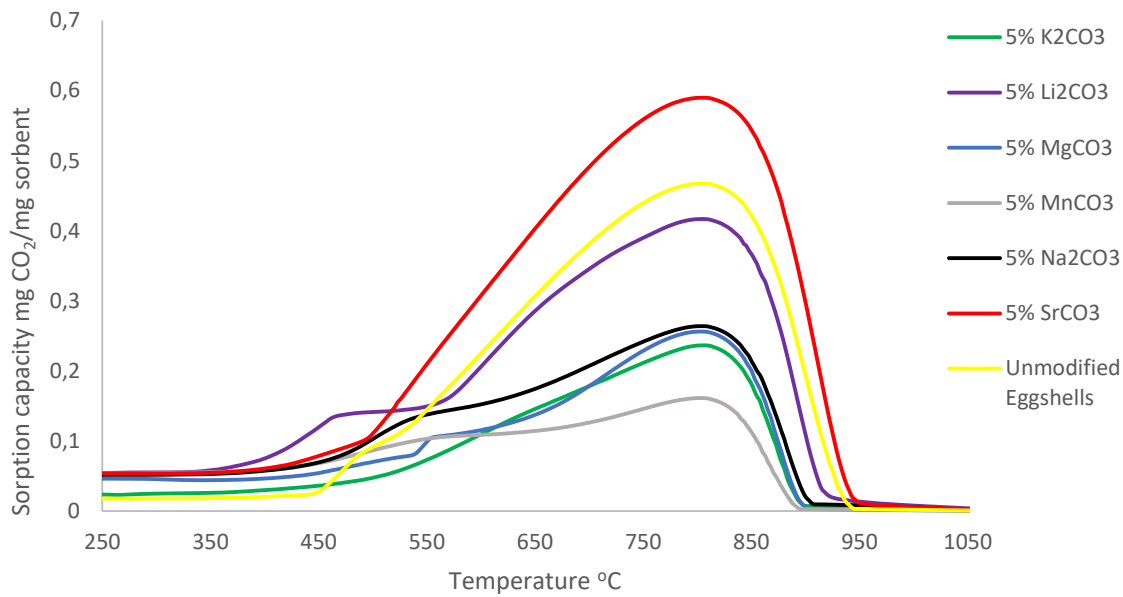


Figure 32 Thermograms of sorbents modified with carbonate salts during dynamic tests

As it can be seen, when we compare sorption capacities captured per mass of a sorbent, only small part of sorbents exceeded calcined raw material sorption capacity. Calcined eggshells achieved their maximum sorbed at 0.46mg CO₂/mg of sorbent. Only two of investigated modifications exceeded this level, modification by zirconia oxide, to 0.61 mg CO₂/mg sorbent and strontium carbonate to 0,59 mg CO₂/mg sorbent. as an explanation of this phenomenon, there is a correlation between the size of the molecule, together with expanded specific surface area and porosity of mentioned material gives results in the better performance. This performance, however, are the overall performances for the total mass of a sorbent, what can be seen especially when we will compare all of the samples prepared with zirconia oxide as a modifier in different ratio. For zirconia oxide modified sorbents, their performances were recalculated with respect to CaO present in the material. All of the sorption capacities were recalculated to form mg CO₂ sorbed/mg of CaO in sorbent. For this purpose, it was assumed, that raw eggshells consist only of CaCO₃ and decomposes completely. The results are presented in the graph below:

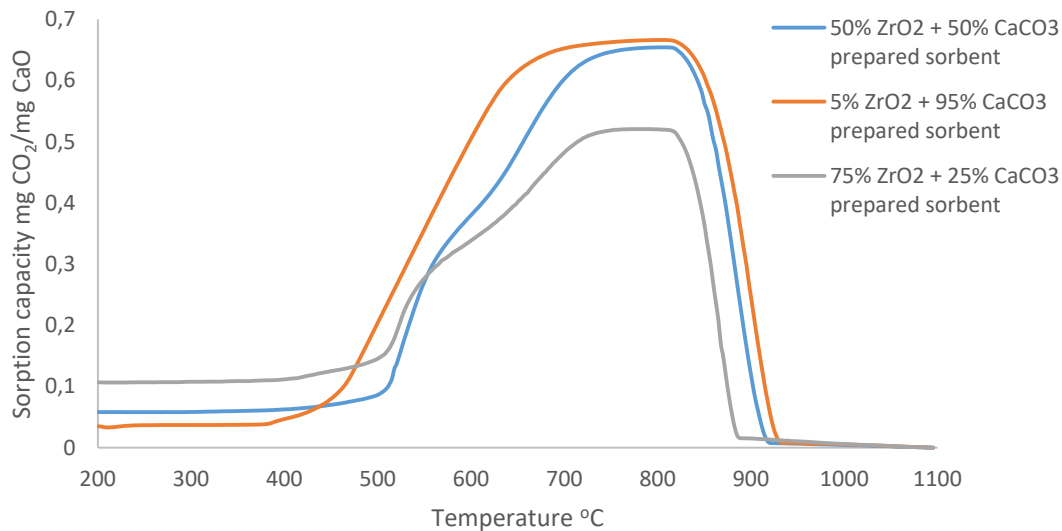


Figure 33 Sorption capacity with respect to mg CaO for sorbents prepared with ZrO₂

Comparing these three prepared sorbents, one may see, that significant change of composition does not change CaO utilization during sorption. Comparing curves it may be seen, that still capture is at the very high level, very close to theoretical maximum uptake by CaO, equal to 0.786 mg CO₂/mg CaO. The only sample with the biggest amount of ZrO₂ decreased capture level to 0.52 mg CO₂. What changed is a rate of carbonation throughout the temperature change.

Another interesting result is a comparison between two samples, which were prepared from the same raw materials, but by different methods. Samples made of eggshells and 5% of SiO₂ were prepared by mixing and grinding both powders, while the second was prepared by means of sol-gel like method. As it turned out, dry mixing has not improved significantly sorption capacity as sol-gel like method did. This might be explained by a fact, that lactic acid, used for solubilisation, increased surface area and pore volume of sorbent particles.

Interesting from the reaction conditions point of view are DTG diagrams, which allows to determine temperature regions, which favours CO₂ capture and decarbonation of sorbent. The results are presented below.

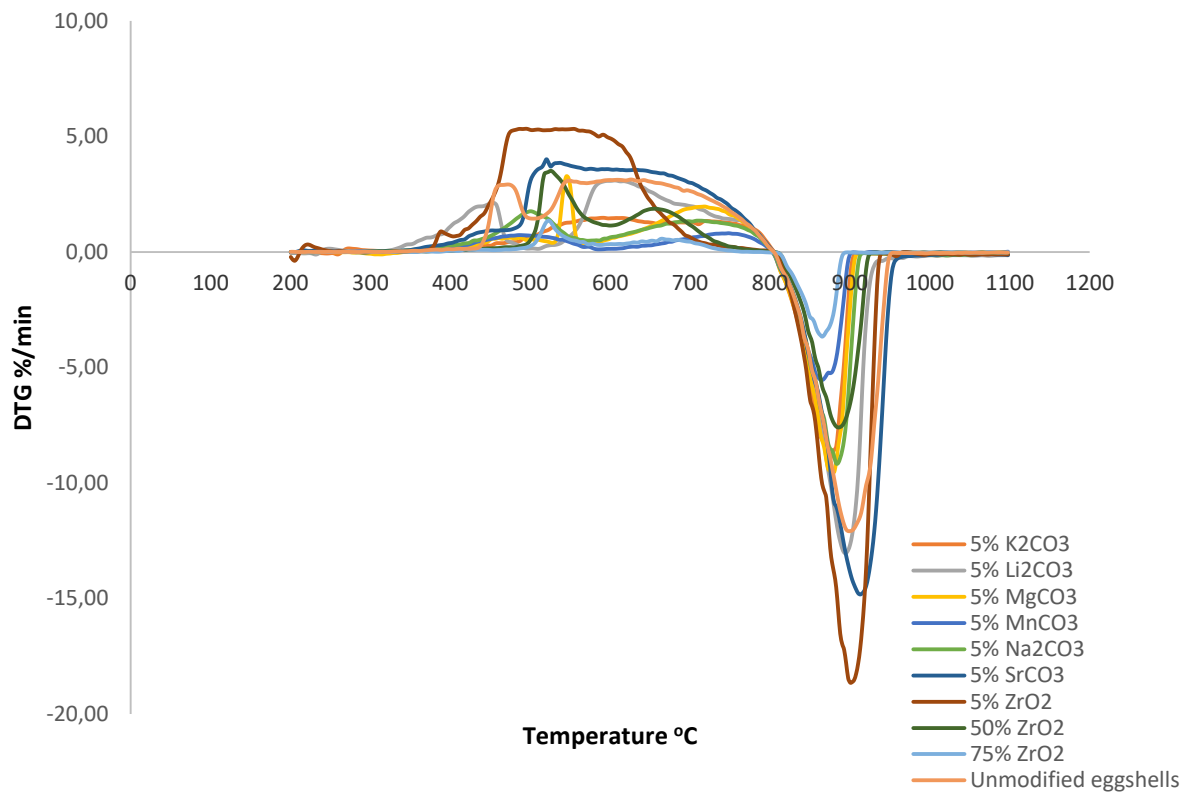


Figure 34 DTG graphs for dynamic tests

What can be noticed is the fact, that carbonation of a samples occurs very quickly, in temperature range starting from 450 °C and, in the majority of samples, sustains at the same level until it achieves temperature 685 °C. Then, the capture rate is slowing down significantly, up to 800 °C, when decarbonation of samples starts. This behavior is caused by the start of the sorption at very low temperature with the kinetic regime, where treated samples were sorbing CO₂ by means of chemical reaction with CaO particles on the surface of sorbent. At the moment, when CaO on the surface is no longer available, CO₂ permeates through the surface of a new formed CaCO₃. This process is significantly slower when comparing to the kinetic stage of a process. In the case of dynamic sorption, we can say, that the process itself does not occur because of the temperature at which the sorbent was, rather it should be considered as a result of kinetic stage termination due to all of the surfaces CaO particles already reacted. In fact, temperature range from 600 up to 800 °C can be used for carbonation process and higher temperature favors higher conversion of CaO to CaCO₃.

When it comes to decarbonation, all of the samples shown drastic loss of mass at 850 °C. This is the minimal temperature, which can be used for decarbonation of CaO sorbents and allows to almost completely decompose CaCO₃ formed to CO₂ and CaO. In theory, this temperature is sufficient to decay CaCO₃, however, higher temperatures are often used in order to reactivate sorbent in high temperature.

CO₂ adsorption test in multicycle experiments.

The main issue regarding calcium looping cycle is to decrease the rate, with which sorbent loses its activity through next cycles of carbonation and decarbonation. A significant decrease of activity loss rate is one of the major issues regarding the commercial application of the sorbent in CCS systems. The

approach applied in this work is to modify the structure of a sorbent in a way, in which not only initial sorption capacity will be increased, but also it will sustain at the satisfactory level throughout multiple cycles. The performance of the sorbent is provided in terms of sorption capacity, noted as a ratio between adsorbed CO₂ per mass of a fresh sorbent. The result is provided as mg CO₂/mg sorbent, and it is calculated as follows.

$$\text{Sorption capacity} = \frac{\text{mass of CO}_2 \text{ sorbed}}{\text{mass of sorbent}}$$

If it is not stated, that condition of performing experiment changed, following conditions of experiment performance were used:

Table 6 Longrun test experimental conditions

Stage	Parameter	Value
Carbonation	Temperature	750 °C
	Time of Reaction	1500 s
	CO ₂ flow rate	20 (%V/V)
	N ₂ flow rate	80 (%V/V)
Decarbonation	Temperature	850 °C
	Time of Reaction	600 s
	CO ₂ flow rate	20 (%V/V)
	N ₂ flow rate	80 (%V/V)
Heating rate		50 °C/min
Cooling rate		25 °C/min
Number of cycles		12

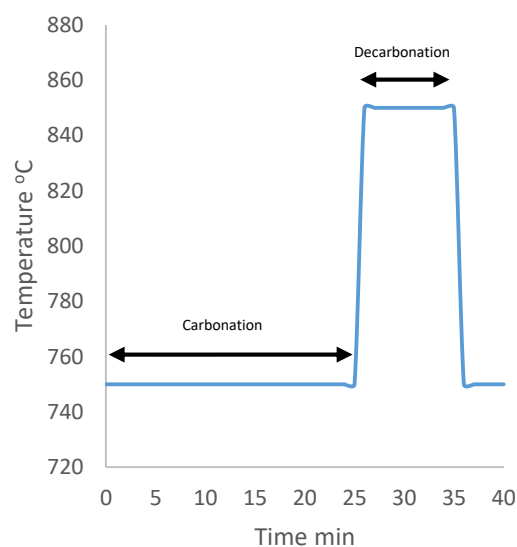


Figure 35 Graphical representation of conditions during longruns

Influence on performance of modifications applied

The most important objective of the thesis was to determine the most appropriate modifier to use for sorbents derived from eggshells. In order to do this, the TGA test was performed for all of the samples and their results were compared. After longrun tests, in order to better understand changes, after test sorbents were subjected to observation using SEM. This procedure allowed to better understand changes occurring on the surface, allowed to compare between specific samples and indicate the reason for different sorbents performances.

Effect of carbonate salts modification on sorbent performance

One of the groups of sorbent, which was prepared and taken into closer consideration, were carbonate salts of metals, such as lithium, sodium, potassium, magnesium, strontium and manganese. All of the mentioned sorbents were subjected to the test performed on thermogravimetric balance, under conditions mentioned in Table 6.

The main issue regarding carbonate modifiers used for investigations is a fact, that they are also decomposing in a similar manner as calcium carbonate, so that into metal oxide and CO₂. Depending on a metal, the temperature of decomposition is different. For proposed temperature of decarbonation, strontium and potassium carbonate are not suspected to decompose, their decomposition occurs at temperatures above 1000 °C. This fact can have a dramatic effect on sorbent performance. Lower decomposition temperature leads to decrease actual surface of a molecule and also causing, that modifier is taking part in the carbonation-decarbonation cycle to some extent. The most desirable situation is when carbonate salt is stable and does not decompose in proposed range of decarbonation-carbonation cycle, and theoretically, these ones should have the best performance. Gathered results for all of the longrun experiments are collected on a graph below.

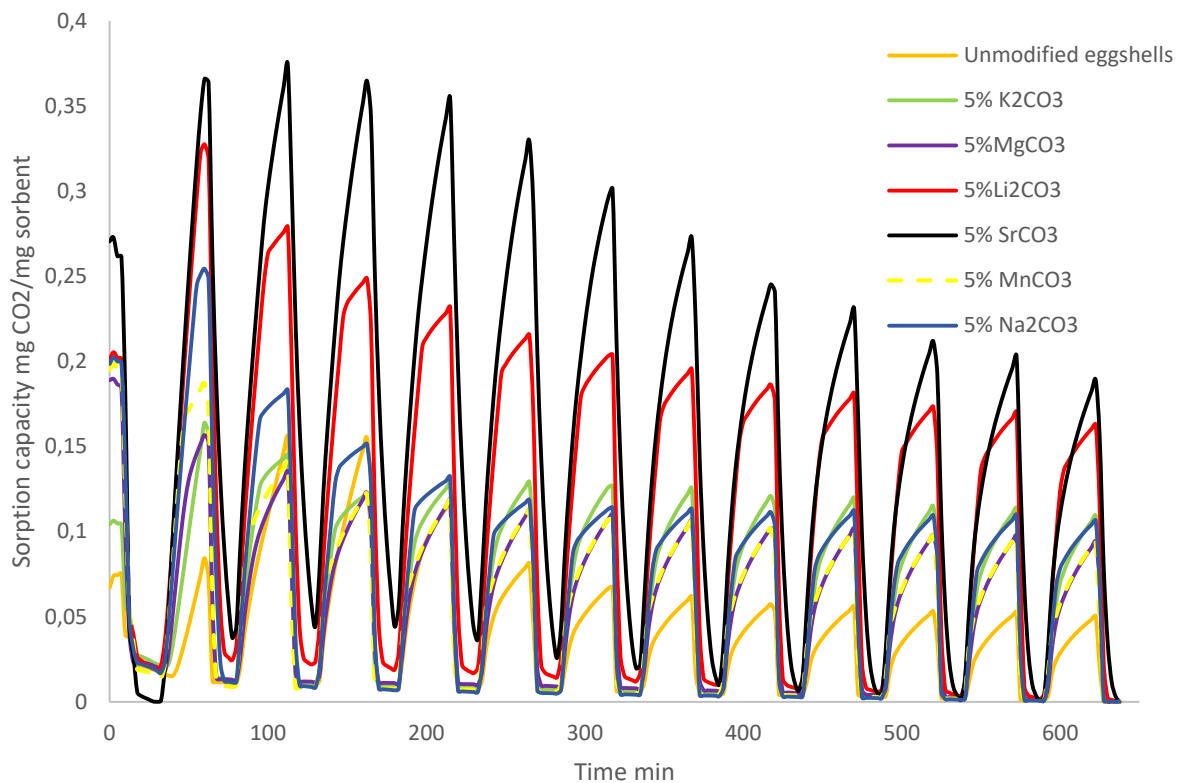


Figure 36 Thermograms for carbonate modified sorbents during longruns

It can be unequivocally said, that all of the modifications used for enhancing the sorption capacity had a positive effect on the process. Some of the examined samples suffered a lower uptake at the beginning of a long run, however, a decrease of capacity is significantly slower than in the case of calcined raw material. Noteworthy is a fact, that except MnCO₃ modified sorbent, none of the samples have reached maximum sorption capacity determined in dynamic sorption. Comparison between sorption capacities from dynamic sorption, first two and last cycle are provided in the table below.

Table 7 Gathered sorption capacities obtained for carbonate modified sorbents

Modifier	Max. sorption in dynamic inv.	1st cycle	2nd cycle	last cycle
SrCO ₃	0.58	0.36	0.37	0.19
MgCO ₃	0.25	0.15	0.14	0.09
K ₂ CO ₃	0.23	0.16	0.14	0.11
MnCO ₃	0.16	0.19*	0.14	0.09
Na ₂ CO ₃	0.26	0.25	0.18	0.11
Li ₂ CO ₃	0.41	0.32	0.28	0.16
Unmodified	0.46	0.08	0.15	0.05

The sorbents, which have achieved the smallest improvement comparing to calcined eggshells are ones modified with magnesium, potassium and manganese. Their sorption capacities at the first three cycles were even worse than the unmodified material, however, this modification allowed to obtain the stable level of sorption capacity as the process proceeded up to the last cycle. It may be concluded, that this stabilization of uptakes is possible throughout the bigger number of cycles, since for manganese and magnesium modified materials there was almost no difference between cycles 4 and 12 and the sorption capacities were maintained at the level of 0.1 mg CO₂ captured per mg of sorbent. Slightly better results are observed when we take potassium modification into account. In this case, sorption capacity was oscillating around 0.115 mg CO₂/mg sorbent. This minor difference can be justified by other nature of a sorbent itself, among all of the three mentioned, potassium carbonate was the only one salt, which has not decomposed during pre-treatment calcination, however, the results for this particular sorbent were slightly below the expectations.

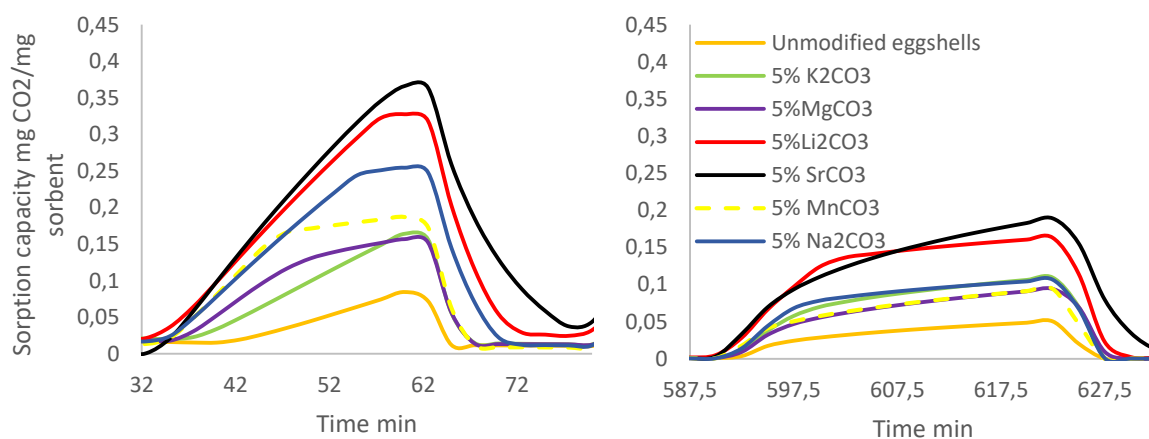


Figure 37 Capture rate profiles during first (left) and last (right) cycle for carbonate modified sorbents longrums

As it can be seen, among all of the examined modifiers, the best influence on sorption capacity increase has strontium carbonate. During all of the carbonation steps, uptake of CO₂ is rapid and kinetic stage is longer than in the case of other modifications. CO₂ uptake at the first cycles is very high and in fact, it was the biggest uptake among all of the multicycle experiments, equal to 0.37 mg CO₂/mg sorbent. On the other hand, a significant issue is a constant decrease of sorption capacity throughout all cycles, resulting 48% decrease when comparing 2nd and 12th cycle. It can be suspected, that during cycles we have not achieved the maximum sorption capacity during the kinetic stage, since the process was kept in the kinetic stage. There exist a possibility, that increased carbonation time will result in bigger uptake of CO₂, thus increase of carbonation time should be investigated.

When it comes to sorbent modified with Li₂CO₃, also reasonably high uptakes were observed, starting from 0,35 at the first cycle and ending up with 0.16 mg CO₂/mg sorbent. What can be noticed, is a different behaviour of a sorbent during consecutive cycles. While the first carbonation cycle is similar to corresponding graphs, following next ones are exhibiting distinct two phases of carbonation. The first one, corresponding to kinetic stage of a process, is very rapid and terminates after 12 minutes and the second phase, diffusive stage, occur. In this case, it can be closely connected with decreased surface area, where the kinetic process is rapid and occur on the surface until the end of available CaO sites. When they terminate, diffusion stage occurs, what leads to decrease the rate of reaction.

When taking a look on sorbents modified by Li₂CO₃ it can be noticed, that after longrun test agglomerates with reasonable sizes are formed. Their structure, however, is very complex and bulk of voids can be noticed. This is one of the possible explanations of fast diffusion stage occurrence. CO₂, in order to penetrate the particle, needs to permeate through it, what decreases significantly rate of the process, however, the surface area is still at the level, which allows to bond significant amounts of carbon dioxide. In the case of SrCO₃ modification, agglomerates are smaller, what gives surface area satisfactory for carbonation process and easily accessible, what is justified by differences in capture rate between Li₂CO₃ and SrCO₃. At first stage capture with Li₂CO₃ is faster, however, due to termination of outer surface enters the diffusional stage. As SrCO₃ was investigated, the rate of capture was slower at first stage, but since it was more stable with respect to time, bigger uptake was achieved.

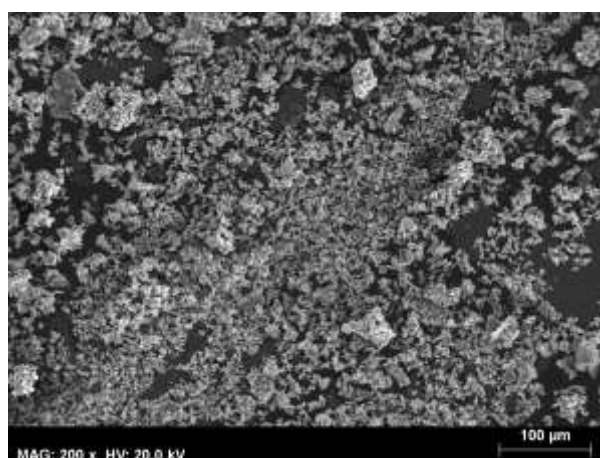


Figure 38 SEM image of unmodified eggshells after 12th cycles of longrun tests

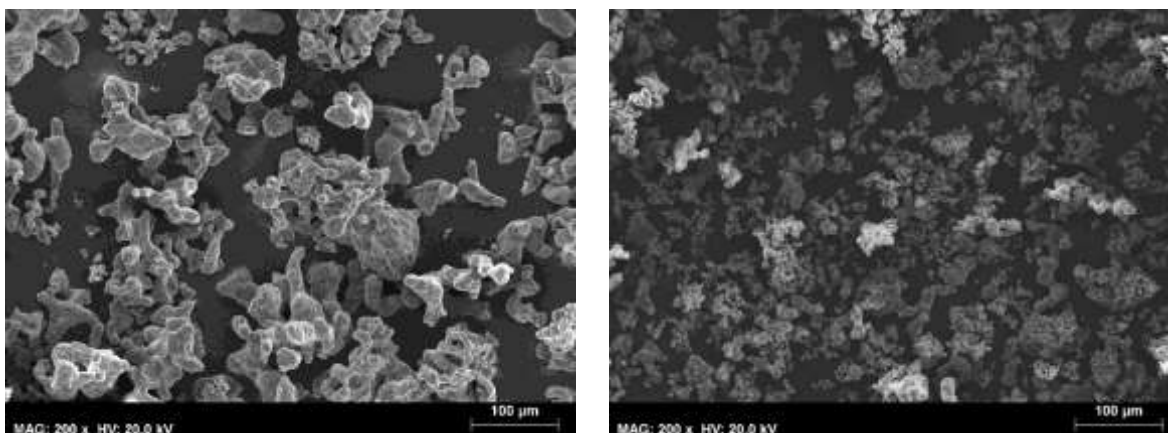


Figure 39 SEM images of Li_2CO_3 (left) and SrCO_3 (right) modified sorbents after longrun

When comparing materials, which achieved significantly smaller performances during longrun tests, some of the common effects of carbonation-decarbonation cycles can be observed. All of these sorbents present tendency to form big agglomerates and particles, from which these agglomerates are formed have a smooth surface. This is caused by attrition of particles and seriously influences sorption capacity, as it can be seen on specific thermograms. It is suspected, that attrition will contribute even bigger into surface degradation, when larger scale fluidized bed is applied. Interaction of sorbent particles and bed in fluidization state may promote faster attrition, what, connected with the negative effect of sintering, may lead to quick sorbent inactivation.

Attrition is especially noticeable on K_2CO_3 modified sorbent image. In the left top corner, particle can be observed, which pores were under degradation, what led to minimize their volume.

As for MgCO_3 modified sorbent, the presence of long structures can be observed. These ones are connected with formation and decomposition of MgCO_3 as standalone particles which do not modify sorbent itself, rather they participate in carbonation-decarbonation cycle. In fact, this modification, comparing to longrun tests performed on dolomite by Li et al. [78] have not achieved good results. The conclusion can be made, that crystallinity of this mineral affects sorption capacity to a greater extent and it is not possible for an artificial mixture of calcium and magnesium carbonates.

Na_2CO_3 modification had not improved sorption capacity both at the beginning of the process as well as at the end of longrun. Particles after tests agglomerated to great extent, forming structures with big voidages inside them. This phenomenon affects sorption capacity and significantly reduces uptakes made by this sorbent.

MnCO_3 sorbents presented a tendency to form big agglomerates, which, together with the attrition of particles, which take part in sintering lead to a decrease of surface area available for CO_2 capture.

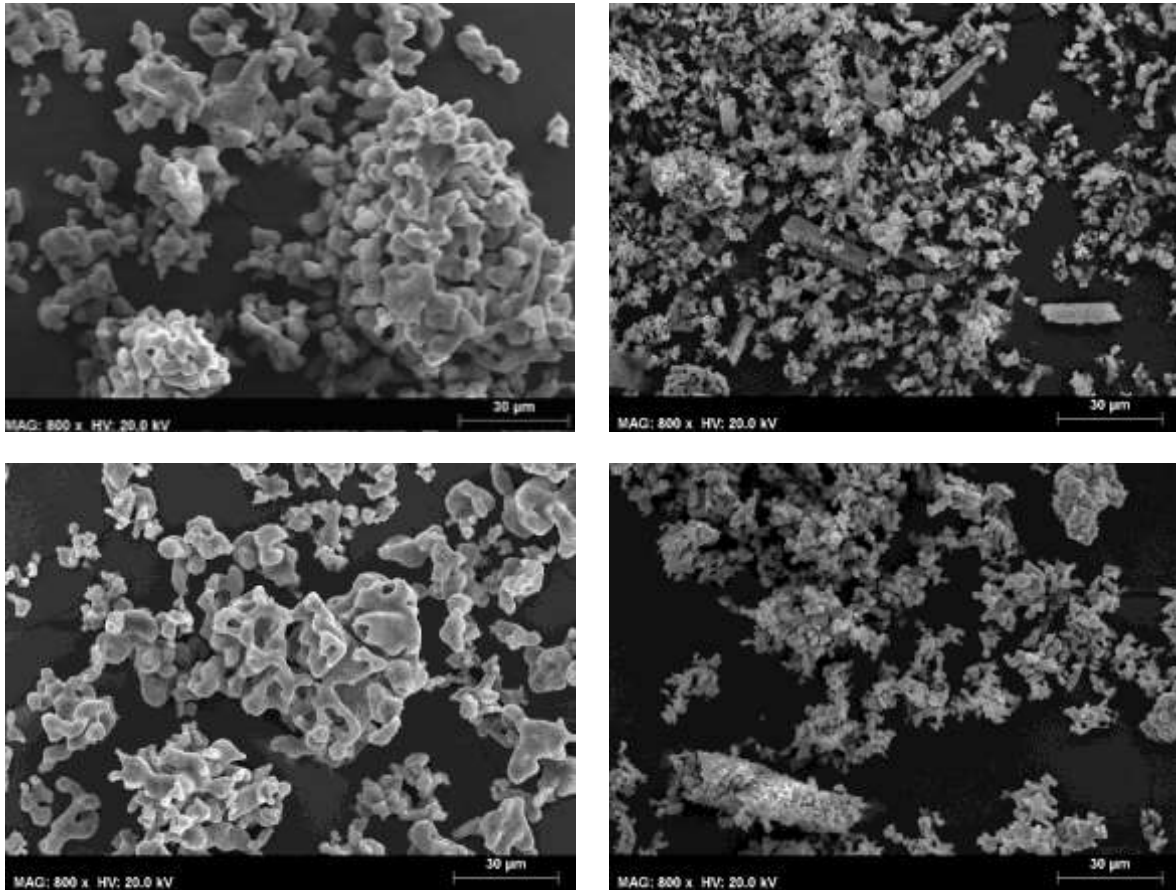


Figure 40 SEM images of K_2CO_3 (left top), $MgCO_3$ (right top), Na_2CO_3 (left bottom) and $MnCO_3$ (right bottom) modified sorbents after longrun

Performance of sorbents prepared by modification with lactic acid

Apart from dry mixing and grinding in mortar, the second method of sorbent preparation was applied. The aim of this procedure was to additionally enhance the surface of the sorbent created during application of sol-gel like method. Results of this type of sorbent long run test are collected on the graph below.

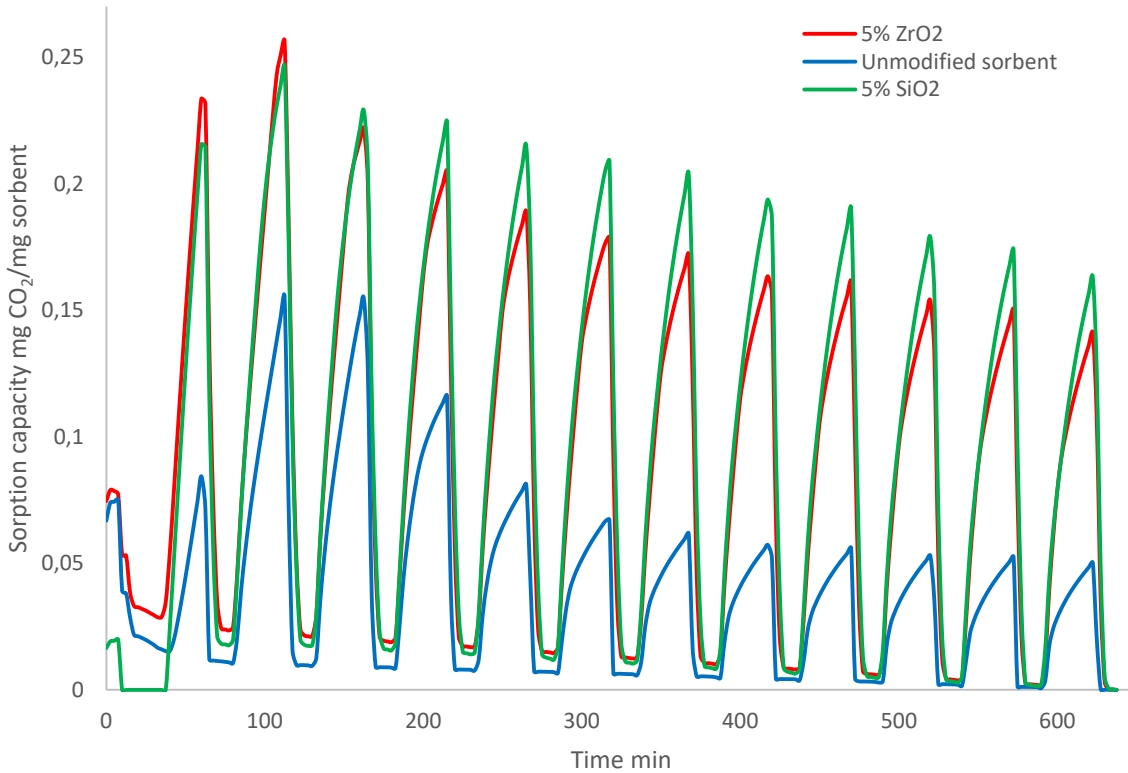


Figure 41 Thermograms for sorbents prepared by sol-gel like method after longruns

Comparing results obtained by examination of sol-gel like prepared sorbents, significant improvement of the sorption capacity among all of the cycles can be observed. Sorption capacities at 1st and the 2nd cycle were bigger 3 and 2 times respectively, while at the last cycle sorption capacity for SiO₂ and ZrO₂ modified sorbents were 500 and 350% bigger.

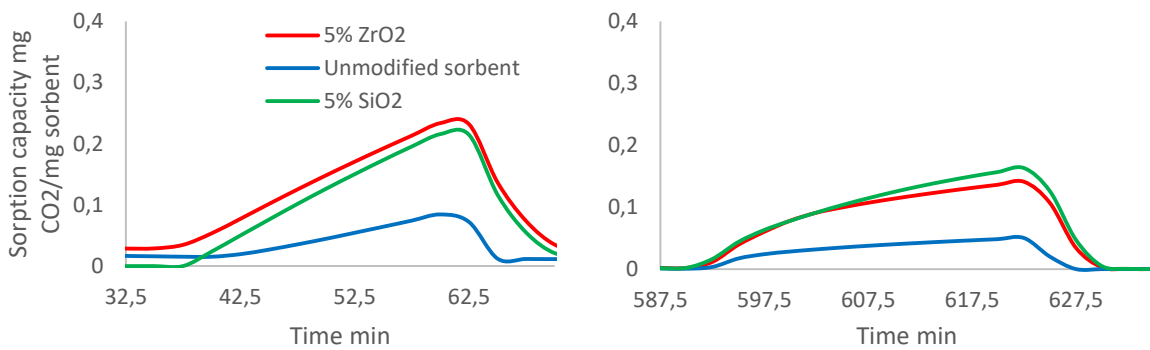


Figure 42 Capture rate profiles for first (left) and last cycle during longruns of sol-gel like prepared sorbents

On figures we can observe the evolution of sorption profile throughout all cycles. As for the first cycles change is constant and relatively rapid for modified sorbents, but during last cycles, rapid sorption is very short, present at the beginning. After the short kinetic stage, diffusional occurs, with significantly

slower capture rate than at the beginning of the process.

Table 8 Gathered sorption capacities obtained for sol-gel like modified sorbents

Sorbent	Max. sorption in dynamic inv.	1 st cycle	2 nd cycle	last cycle
SiO ₂	0.32	0.21	0.24	0.16
ZrO ₂	0.61	0.23	0.26	0.14
Unmodified eggshells	0.46	0.08	0.15	0.05

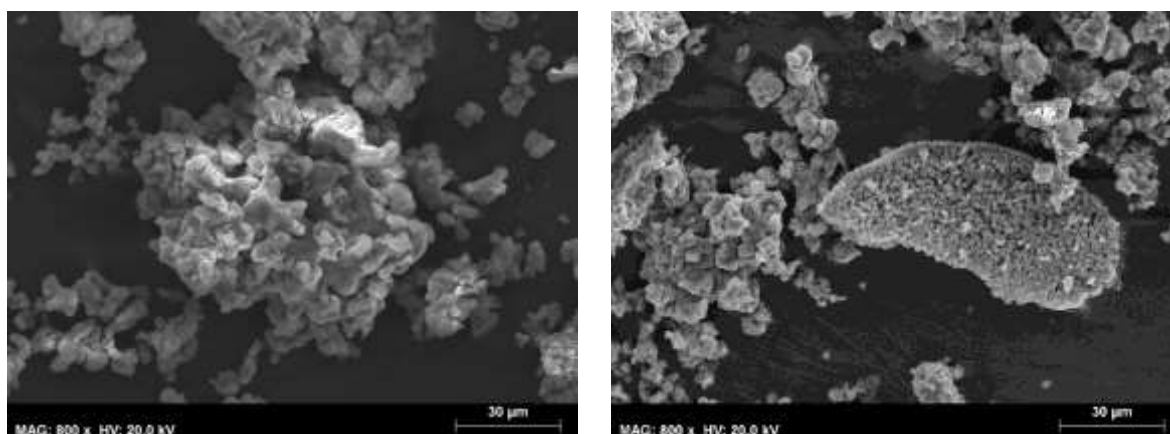


Figure 43 SEM images of ZrO₂ (left) and SiO₂ (right) modified sorbents prepared by sol-gel like method

As it can be seen on SEM images, both sorbents present development of complex surfaces with pores even after longrun tests. It can be stated, that this is caused by the process of preparation itself. The way of preparation allowed to obtain a uniform distribution of modifier among whole prepared sorbent, what caused coverage of modifier by calcium lactate, which during calcination decomposed, creating reasonably bigger surface area beneficial for further CO₂ capture.

Influence of decarbonation time on sorbent regenerability

Since sorption capacity decreases during consecutive cycles and the rate is changing constantly, the decision was made to perform decarbonation time influence on the CO₂ uptake. Longer time of residence in higher temperature can lead to faster degradation of sorbent surface, what leads to decrease of sorption capacity. When considering a continuous operation on the same sorbent, it is reasonable to check whether increased decarbonation time influences the sorption capacity for a given sorbent. The

test consisted of 4 long run tests performed on two modified sorbents, one with 5% ZrO_2 and second with 5% $SrCO_3$. The first test was performed with standard conditions mentioned in Table 6, while in second decarbonation time was extended to 25 minutes. Results of these comparisons are collected on pictures below.

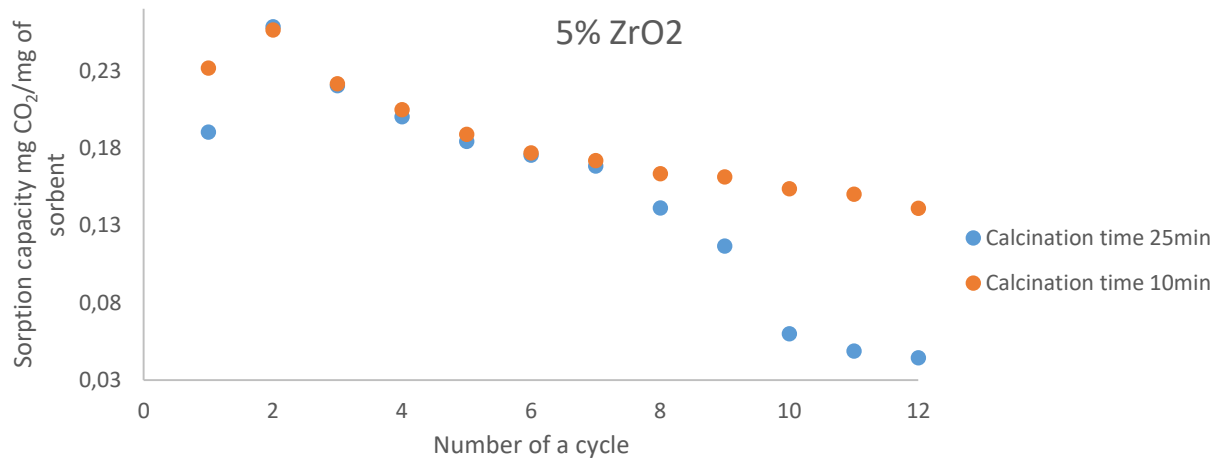


Figure 44 Evolution of sorption capacity for ZrO_2 modified sorbents vs. number of a cycle

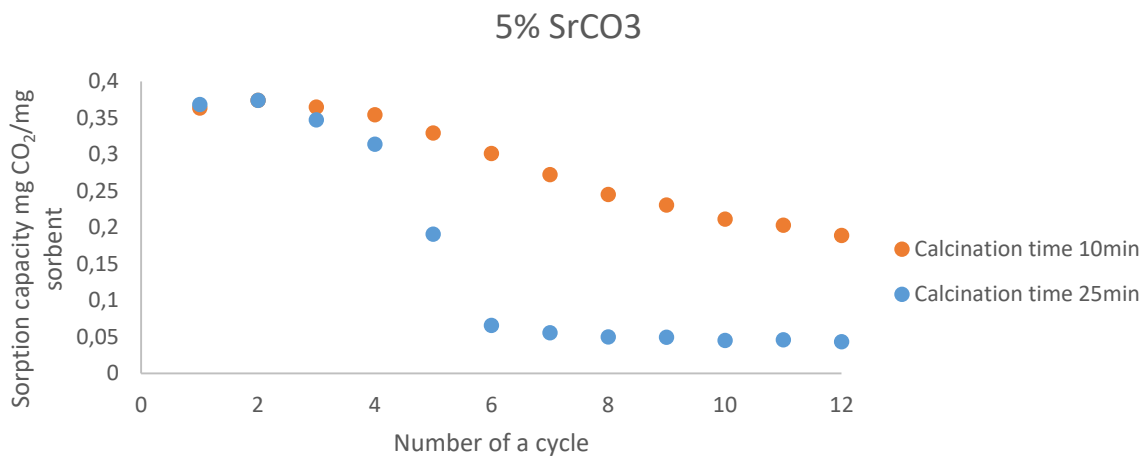


Figure 45 Evolution of sorption capacity for $SrCO_3$ modified sorbents vs. number of a cycle

For both type of sorbents decrease of CO_2 uptake was observed. While at the beginning of long run tests sorption capacities observed are at similar levels, the more cycles were applied, the difference between runs is bigger. It is especially visible when 5% $SrCO_3$ sorbent is taken into account, where at 6th cycle decrease to 0,05 mg CO_2 /mg sorbent is observed. For ZrO_2 modified sorbent the effect of increased decarbonation time is less drastic, where a significant drop of sorption capacity is observed during 10th cycle. this difference can be explained by different sorbent preparation method. For ZrO_2 modification, sol-gel like method was applied. It is reasonable to state, that this method allows creating sorbent, which is more resistant to harsh conditions of the process.

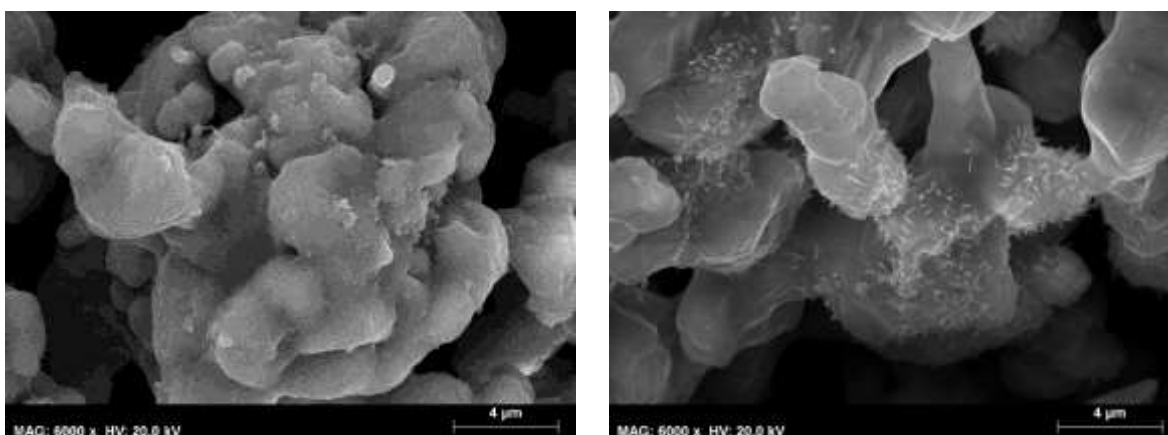


Figure 46 SEM images of SrCO_3 modified sorbents after longruns (left - longer calcination time, right - shorter calcination time)

As it can be seen on SEM images of SrCO_3 modified sorbents, longer decarbonation time affected significantly surface of the sorbent. Sample taken after 25min decarbonation cycle have attrited to a greater extent and formed bigger agglomerates, however, there are some pores, which can be penetrated by usage of longer carbonation time. When looking on sorbent with 10min decarbonation step, the surface is definitely more complex, covered by thin, long needle-like structures, which most probable origin is SrCO_3 crystals (the structure is similar to one described in morphological consideration made by Alavi and Morsali in [56]) covered by CaO . This may justify better performance achieved in this experiment and allows to think, that examined conditions with 10 minutes decarbonation time can be successfully applied for longer run experiments.

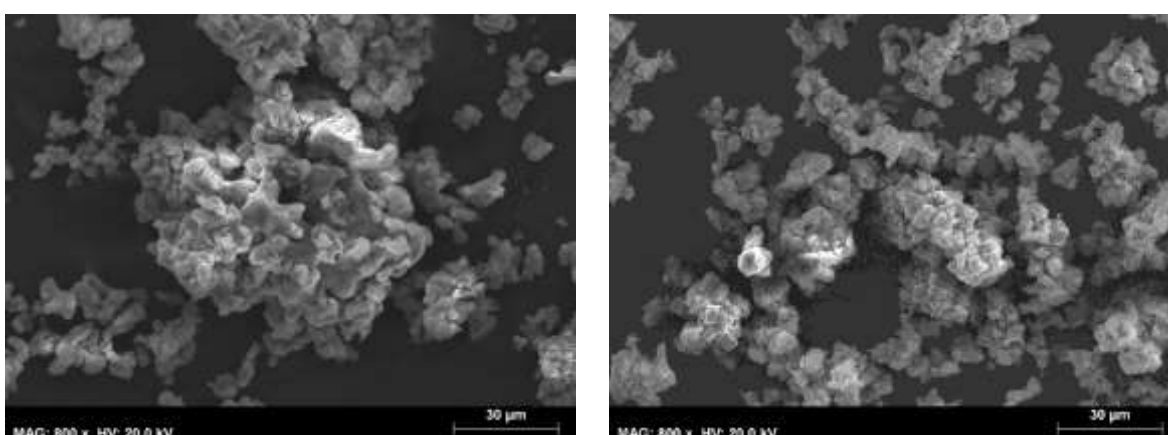


Figure 47 SEM images of ZrO_2 modified sorbents after longruns (left - longer calcination time, right - shorter calcination time)

When it comes to ZrO_2 , one of the main conclusions made by investigating SEM images is higher sintering of particles. Clustering in case of longer calcination progressed to larger extent, however, agglomerates have still complex shape of a surface. As it was stated earlier, lower advancement of

sorbent deactivation might be connected with sorbent preparation method, what significantly improved resistance to conditions.

For determination of the best conditions to capture CO₂, decarbonation time should be limited to an absolute minimum, in order to prevent faster surface degradation.

Influence of sorption preparation method on performance

In order to determine, which method of sorbent improvement is more suitable for increase of CO₂ uptake in long run experiments, two versions of silicon oxide modified sorbents were tested, one, prepared by dry mixing of SiO₂ with eggshells, and second, with the same reagent, prepared by sol-gel like method with addition of lactic acid. Resulting thermograms are presented in a chart below.

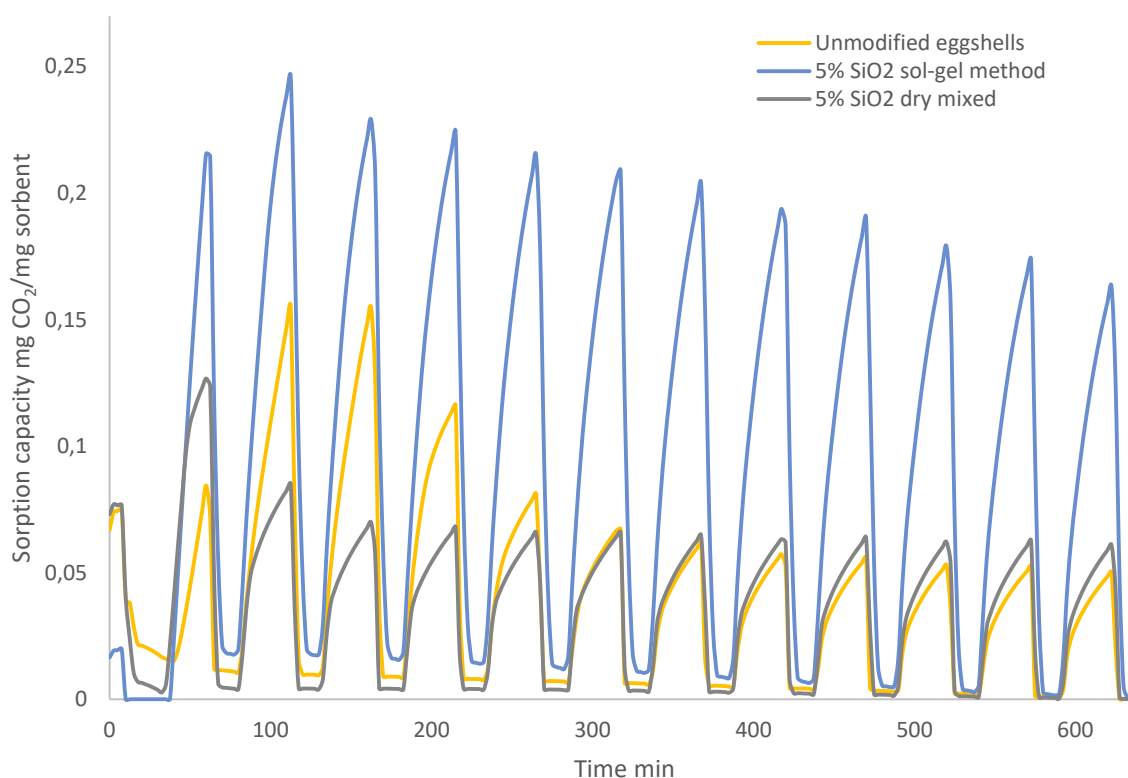


Figure 48 Thermograms of sorbents prepared by modification with SiO₂

Having in mind, that in dynamic tests sol-gel like modified sorbent had a slightly better performance from dry mixed one (0,32 vs 0,24 mg CO₂/mg sorbent), it is not surprising, that this samples exhibited much better performance than the second one. However, the effect of sorbent preparation method in this particular case has a dramatic effect on sorption capacity starting from the first cycles, up to the end of the test. Dry mixed eggshells with SiO₂ have not even increase sorption capacity at initial stages, having better results than untreated calcined eggshells from the 9th cycle and even then, the improvement was very small, 0,01 mg CO₂/mg sorbent. Considering maximum sorption capacity achieved in the dynamic test, only 50% of maximum was achieved, comparing to 78% by impregnated one.

Also noteworthy is fact, how the kinetics of sorption looks like. In the case of sol-gel like treated sorbent capture is performed with very rapid rate, same as in the kinetic stage of the process, while dry mixed after very short time of this stage is entering into the diffusional stage, which is maintained by the majority

of carbonation time. This is closely related to porosity and specific surface area, which, when comparing both samples, is in favour of the sample prepared by sol-gel like method. Decreased surface area leads to faster utilization of surface CaO, what leads to the prolonged diffusional stage, in which rate of CO₂ capture is significantly slower.

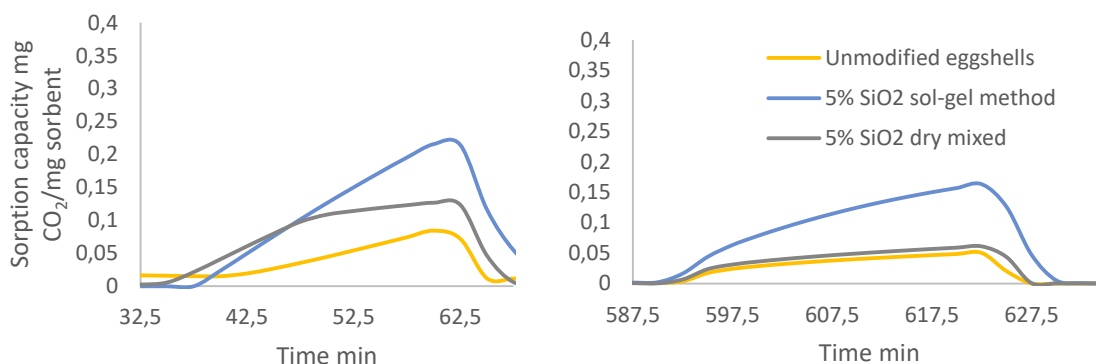


Figure 49 Capture rate profiles of SiO₂ modified sorbents during first (left) and last (right) cycle

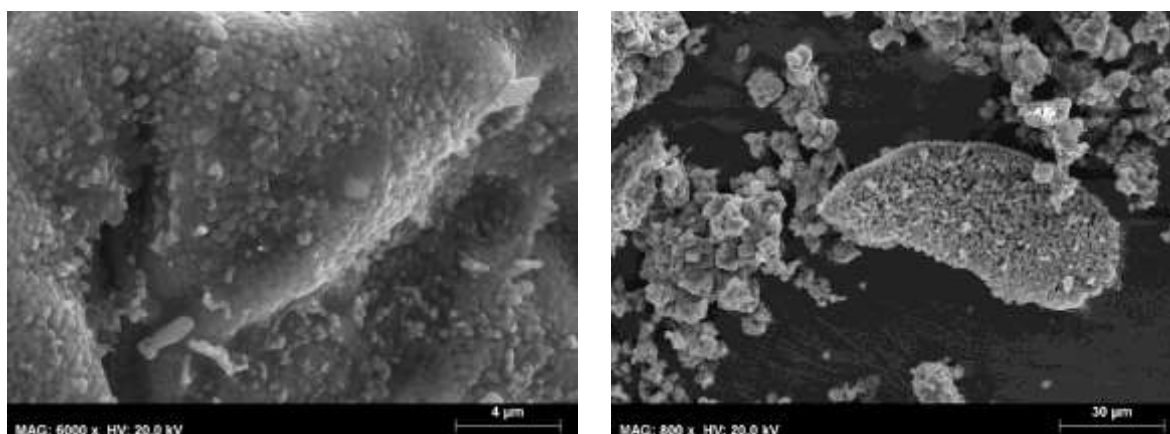


Figure 50 SEM images of dry-mixed SiO₂ modified sorbent (left) and using sol-gel like method (right)

Table 9 Gathered sorption capacities obtained for SiO₂ modified sorbents

Sorbent	Max. sorption in dynamic inv.	1 st cycle	2 nd cycle	last cycle
Sol-gel like	0.32	0.21	0.24	0.16
Dry mixed	0.24	0.12	0.08	0.06
Unmodified eggshells	0.46	0.08	0.15	0.05

As comparing morphologies of both materials, a significant difference between both of them can be observed. On material prepared by dry mixing, it is visible, that sinterization of material is very advanced after 12th cycles and representing almost no pores. Particles are representing enormous agglomeration,

what can be observed on particles' surface, which in fact consist of a lot of smaller particles connected into one bigger, with no pores and almost no complexity observed. It is completely adverse effect as for sample prepared by usage of lactic acid. In this case, agglomerates also occur, however, their surfaces are much more complex and one can notice voids between sintered particles, which results in bigger calcium oxide availability, thus bigger sorption capacities are obtained. This difference can be explained by calcium lactate formation during sorbent preparation. When calcined, this compound decomposes and creates surface composed of calcium oxide with a positive impact on the specific surface area. It may be concluded, that surface of the lactic acid prepared sorbent can sustain bigger sorption capacities than preparing them by mixing with modifier only.

Longrun experiment performed for 25 cycles

In order to determine sorbents' behavior in longer cycles, in specific, if the constant decrease of sorption capacity is observed and if there exist the possibility to obtain the self-regeneration effect, examination by TGA apparatus was applied. The conditions of experiment remained the same as noted in Table 6, but instead of 10 consecutive carbonation-decarbonation cycles, 23 were applied. For this type investigation two of the best sorbents prepared by each method were chosen, namely modified with 5% SrCO₃ by dry mixing method and 5% SiO₂ by means of sol-gel like method. As a reference, unmodified eggshells sorbent was examined in the same conditions. Resulted thermograms are presented in Figure 51.

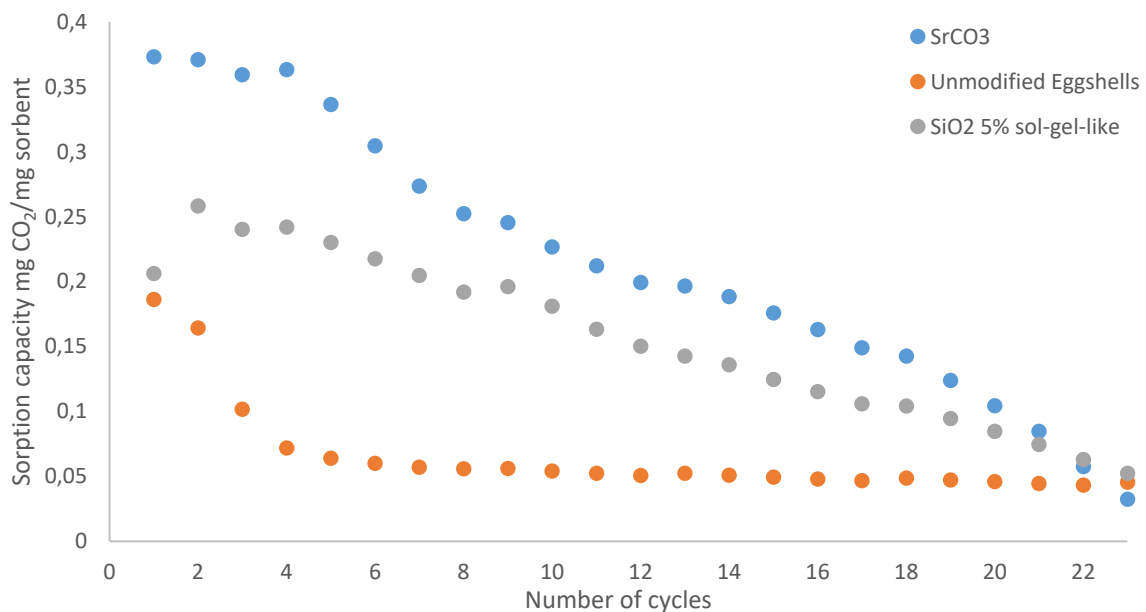


Figure 51 Evolution of sorption capacity with increase of cycle number

As it can be seen on thermograms, unmodified eggshells sorbent retains the sorption capacity after the fourth carbonation cycle. This sorbent is very stable even though its CO₂ sorption capacity is not at satisfactory level. A different behavior trend was observed for the SiO₂ and SrCO₃ modified sorbents. In these cases, uptakes are subjected to continuous decrease. An especially sample modified with SrCO₃ suffered a dramatic decrease of sorption capacity, which results in CO₂ uptake at the lower level than unmodified material at the end of the experiment. It may be concluded, that this modification has

not resulted in increased sintering resistance, causing a sorption capacity decrease to the level of 0,03 mg CO₂/mg sorbent, what is a decrease by 92%. The slightly better performance was exhibited by sample prepared by modification using SiO₂. This sorbent uptake decrease was not as drastic as in the case of previously mentioned modification, however, the difference is still significant. It can be noticed, that in the last cycle its performance is better only by 0,01 mg CO₂/mg sorbent. It can be stated, that this modification makes sorbents more resistant to sintering and attrition, however, it is not on the satisfactory level to assume, that regenerability is at sufficient level to use sorbent for longer cycles.

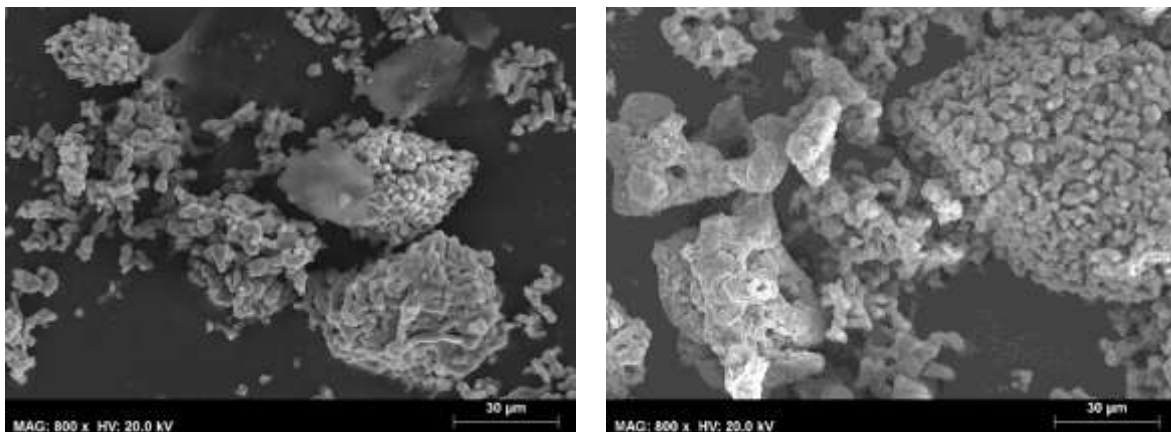


Figure 52 SEM images of unmodified sorbent (left) and modified with 5% SrCO₃, after 23 cycles

When taking a look at SEM images of unmodified calcined eggshells and SrCO₃ modified sorbent, one may see a very advance sintering. Particles are collected into several big agglomerates, poor when it comes to the structure of the surface and pore existence. Also, when taking a look on calcinated eggshells, there exist 2 particles, which one side is sintered to an extent, in which it is impossible to notice smaller grains, from which agglomerate is formed. It is an evidence of drastic degradation of sorbent which happens throughout the calcium looping cycle,

5. Conclusions

The main goal of this thesis was to develop calcium sorbents derived from eggshells, which will be able to capture CO₂. The key properties, which were desired to obtain are satisfactory sorption capacity and decreased sorbent deactivation. These materials can be used as a one of the solutions for rising global warming issues closely related to CO₂ emission by combustion of fossil fuels and solve problems related to other technologies investigated, such as big energy penalty, handling wastes generated throughout the whole process application and similar. It was proved, that eggshells are excellent feedstock for calcium looping cycle sorbents and there are ways to produce enhanced material with good sorption properties influencing chemisorption process, namely surface area, pore volume and attrition and sintering resistance.

Over the time of experiments, several modifiers were examined in terms of their influence on sorbent performance. It was found out, that addition of SrCO₃ and Li₂CO₃ mixed and grinded together with raw material significantly improved sorption capacity, which was sustained at a satisfactory level during multi carbonation-decarbonation cycles. In terms of a way to prepare sorbents, method, which bases on Pechini approach with lactic acid, performed by introducing eggshells and modifier into an aqueous solution, showed significant improvement in terms of CO₂ uptake and better regenerability than samples prepared by dry mixing of feedstock and modifier. Among sorbents prepared by modified sol-gel like method both SiO₂ and ZrO₂ modified sorbents showed good regenerability, while adjustment by silicon oxide gave bigger CO₂ uptakes.

Important from the determination of process conditions point of view was decarbonation time influence on sorbent performances. Increased decarbonation time seriously affected sorbents regenerability by dropping sorption capacities in consecutive stages to a minimum. It appeared, that more resistant to severe decarbonation condition was sorbent prepared by modified Pechini route, what allowed to postpone significant sorption capacity drop to a later number of a cycle.

As proposed modification appears to be a suitable way to enhance performance, further researches should be done. As a recommendation, the influence of Li₂CO₃ and SrCO₃ modification with the usage of modified Pechini route should be investigated if it allows achieving better results. Also, interesting would be a determination of the most suitable amounts of modifiers, as well as using ones with more compounds included.

When it comes to conditions of calcium looping cycle, experiments in a bigger scale with the usage of fluidized bed reactor should be undertaken in order to understand better the changes of particle surface in constant motion. As for decarbonation, attempts of calcination in the CO₂ pure atmosphere should be taken into consideration, as circumstances which fit better to state in which the process will be undertaken.

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