

# Waste Ca (Eggshells) natural materials for CO<sub>2</sub> capture

Krzysztof Trzepizur

## Abstract

The CO<sub>2</sub> produced by fossil fuels combustion is responsible by greenhouse gas effect and consequent global warming. Current international directives are aiming a drastic reduction of CO<sub>2</sub> 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 CO<sub>2</sub> sorption capacity due to sinterization. In fact, the cyclic carbonation/decarbonation occurs at temperatures higher than the CaCO<sub>3</sub> Tamman 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, SiO<sub>2</sub> and ZrO<sub>2</sub>. 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 CO<sub>2</sub> in N<sub>2</sub>, showed that small amounts of dopant elements are able to improve the lime stability, eventually by a monophasic spacer effect. As expected the sol-like process produced more stable sorbents.

**Keywords:** CO<sub>2</sub> capture, post-combustion, CCS, calcium cycle, sinterization, sol-gel

The contribution of anthropogenic greenhouse gases (GHG) to climate change is often considered as the main reason for global warming and increasing annual average temperature. A significant part of GHGs is carbon dioxide – gaseous compound which is a result of fuel combustion. It is responsible for 81% of total GHG emission observed [1]. Especially CO<sub>2</sub> generated by fossil fuel burning affects carbon cycle dramatically, increasing amounts of this gas to a significant level.

There are many environmental incentives which purpose is to decrease a level of GHG emitted to the atmosphere and prevent environment for further damage. To these treaties, we can include Kyoto protocol and COP21, which is the most recent one. Also, there exist an economic solution for large industry CO<sub>2</sub> producers, called cap and trade. All of these solutions have a common goal – decrease amount of GHG emitted and fossil fuel usage for energy generation.

Unfortunately, fossil fuels will be still a dominant energy source in the energy mix [2] and there is a need to develop solutions, which will minimize the impact of carbon dioxide on the global warming. These are named Carbon Capture and Storage technologies (CCS), which purpose is to capture CO<sub>2</sub> formed during combustion, prepare for transportation and store in the appropriate destination, where its impact on the environment will be negligible. CCS is currently investigated by three approaches – pre-combustion, post-combustion and oxy-combustion technologies[3].

There are multiple paths taken into account when it comes to carbon dioxide capture including various techniques [4]. The methods are developed under various means, such as absorption, adsorption, cryogenic separation, biochemical way or membrane separation. The target of the whole methods mentioned is to create two streams of a flue gases, one containing compounds neutral for the environment, such as nitrogen and water and the second, containing concentrated CO<sub>2</sub> for further treatment.

Currently, post-combustion technologies are the most often considered approach for CCS, especially absorption with amine usage. CO<sub>2</sub> is absorbed by a carrier liquid, usually monoethanolamine with efficiency up to 70-80%, then it is delivered to desorber for CO<sub>2</sub> discharge. This method, however, suffers a significant disadvantages, such as corrosive properties of a carrier liquid and high energy penalty caused by solvent regeneration. It is a reason, why other methods are investigated.

One of the most promising methods of CO<sub>2</sub> sequestration is capture by means of adsorption. Currently, there are many sorbents investigated, including activated carbons, zeolites and metalo-organic frameworks. One of the biggest interest for gas-solid adsorption material lies in calcium oxide sorbent materials. The capture is done by means of the well-known reversible reaction of carbonation-calcination reaction:



This material has significant advantages among other investigated materials – it is cheap, abundant, it does not have a major environmental impact, is not toxic and can be used in fluidized bed systems. Calcium oxide for CO<sub>2</sub> capture results in lower energy penalty than amine absorption and it has a capability to bond sulphur oxides as well. Spent sorbent can be used as an additive to construction materials.

There is a collection of materials, which can be used as a raw material for sorbent preparation. Nowadays most examined materials are mineral ones, mainly calcite derived from limestone, but also other rocks, like dolomite and marble. All of the mentioned rocks are characterized by high calcium content, what allows to obtain big calcium content and thus high CO<sub>2</sub> sorption capacity. Also, biogenic sources of Ca were investigated in terms of their potential ability to become reasonable calcium source. Witton [23] was investigating eggshells, while Castillo [7] did an examination of most of the biogenic materials, including seafood shells, like scallops, mussels and snails.

Carbonation of CaO is done in the temperature range of 750-900 °C, while calcination at 900-1100 °C. One of the major issue regarding usage of calcium oxide as a CO<sub>2</sub> sorbent is its drastic decrease of sorption capacity throughout next cycles. Reactivity loss of reagent is often explained by changes in the morphological structure of the material, caused by constant interaction between particles, high temperature and incomplete calcination reaction [5]. All of that phenomenon leads to sintering of a particle, its attrition and loss in surface area.

A lot of efforts were made in order to improve the performance of sorbents, by increase its stability, sintering resistance and sorption capacity. Manovic et al. [8] proposed thermal pretreatment of calcium oxide material and determination of the best residence time and temperature for sorbent preparation. They found out, that processing can help to obtain self-regenerable sorbent. Chen et al. [9] after thermal treatment were able to double sorption capacity of calcium oxide. Another method was the application of hydration, which is used nowadays in FGD systems. Han et al compared liquid and steam hydration of pure calcium oxide [10]. The method resulted in high surface area and porosity, however, increase significantly energy penalty caused by the method. Rong et al justified, that best results are obtained by every cycle hydration at 300 °C [11]. The most extensively examined opportunity for improvements are modifications

using chemical reagents. Li et al was investigating the influence of ethanol/water solution on calcium oxide, finding out, that the bigger ethanol concentration, the better results are [12]. Ridha et al. on the other hand were using formic acid, what resulted in bigger sintering resistance of particles [13], even without increasing pore volume and surface area. After acetic acid though, was giving slight improvement where was applied to samples calcined at lower temperatures [14]. Pyrolygneous acid consisted of both previously mentioned acids was investigated by the same authors [15], where 25% improvement of sorption capacity after 100 cycles was made comparing to the untreated sorbent. On the other hand, for sorbent performance improvement are salts incorporated into the structure of the particle. The purpose of this operation is to enhance particle size, its surface area and make the particle more sintering resistant. Apparently, numbers of different salts were examined in terms of their potential impact on a particle. Salvador et al. [16] were examining the influence of NaCl and Na<sub>2</sub>CO<sub>3</sub> on the reactivity of the material, however, they achieved completely reverse effect of decrease all of the crucial parameters. Another examined materials were 1<sup>st</sup> group metal chlorides by Reddy and Smirniotis [17]. They observed, that wet impregnated materials with analytical grade calcium oxide had better performance when a metal atom in salt was more electropositive. Different manganese salts were examined by Sun et al., founding out, that they do not increase initial sorption capacity, but in longer range of 100 cycles allow to achieve 69% better intakes than pure analytical one. Metal oxides are also checked in terms of sorbent enhancement. Koirala et al. developed flame spray pyrolysis of CaO and doped this compound on calcium zirconium oxide [18]. They have obtained a significant improvement in terms of total conversion after 100 cycles equal to 45%. Broda and Muller on the other hand, using sol-gel method were doping CaO on ZrO<sub>2</sub> [19]. They were using calcium nitrate, hydroxide and acetate as precursors. Materials obtained were characterized by high surface area and pore volume.

Researches of calcium sorbents for CO<sub>2</sub> capture were done using diverse precursors. Apart from analytical grade reagents, in usage were also naturally abundant materials. One of the most extensively examined material was limestone, due to high calcium content, up to 95% [20]. However, other materials like dolomite [21] and waste marble powder from mason industry [22] were examined. Promising raw material are biogenic wastes as well. These

garbage, such as eggshells, cuticles of diverse seafood, are also containing a significant amount of calcium carbonate, which can be used as sorbent precursor. Castillo et al. [7] were examining their applicability for this purpose, examining each one, including cuticles of seafood, snails and eggshells. Researches done proved, that they can be used for CO<sub>2</sub> capture, however, scallops and eggshells have the biggest potential, uptaking bigger amounts of CO<sub>2</sub> than other materials. Witoon [23] examined material in terms of CO<sub>2</sub> capture as well, obtaining material, which after treatment could be an interesting raw material for CO<sub>2</sub> adsorbent.

## Experimental

### Materials

The primary raw material were eggshells collected in households. All of the eggshells were rinsed and then dried. Dry material was crushed with the usage of porcelain, and as a second stage, agate mortar. One group of samples were dry mixed, the second one was prepared using sol-gel like method. The dry mixed group was prepared by grinding precursor and modifier together. Sol-gel like method was performed in water solution. Precursor and modifier were introduced to demineralized water, agitated and heated up to 70 °C. After achieving proper temperature, lactic acid was introduced slowly. After acid addition, agitation was performed during 30 mins, then water was evaporated. The names of examined samples are derived from modifier compound and the corresponding amount of modifier used. Before investigation samples were previously dried if it was necessary and then calcined in 900 °C during 4 hours.

### Characterization of materials

Prepared powders, as well as samples after calcinations were investigated in terms of XRD analysis on Burke D8 Advance X-Ray diffractometer with CuK $\alpha$  radiation at 40 kV and 40 mA. The measurement was taken within the range of 10-75°, 0.02°/s, and then compared with JCPDS patterns. SEM was performed on Hitachi S-2400 on samples coated by a gold-palladium coating.

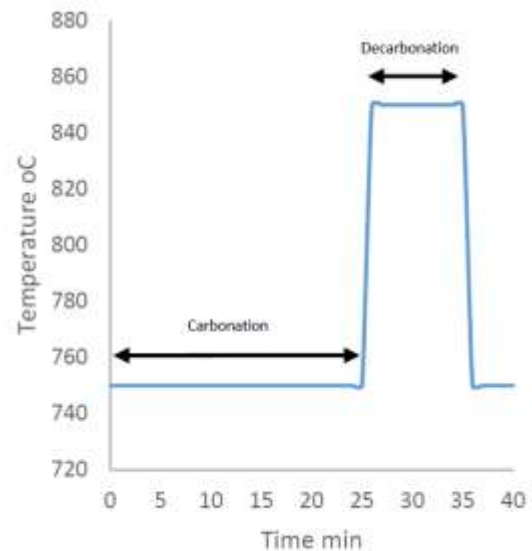


Figure 1 Graphical representation of conditions during longruns

### Thermogravimetric analysis

Adsorption tests on prepared materials were performed using thermal gravimetric analysis. Into the thermobalance used for that purpose samples of adsorbent were introduced, then heated up to the carbonation temperature 750 °C in ratio 50 °C/min. After carbonation-calcination was performed in a temperature of 850 °C. All of the experiments were done in a constant flow of gaseous nitrogen and CO<sub>2</sub> with composition 20% V/V CO<sub>2</sub> and 80% V/V N<sub>2</sub>. One experiment consisted of 10 cycles of carbonation-calcination. The carrying capacity of each sample was determined as the ratio of CO<sub>2</sub> adsorbed to the total mass of the calcined sample. The measurement was made using NETZSCH STA 409 PC coupled with the flow controller.

## Results and discussion

### Influence of carbonate salts on sorbent performance

The main purpose of this modification was to form modifier-CaO agglomerates for enhancement of surface area, what could possibly increase sorption capacity of a given material. Depending on carbonate, four of them (Na<sub>2</sub>CO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub>, MnCO<sub>3</sub>, MgCO<sub>3</sub>) were suspected to decompose during pre-calcination of material, while SrCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> are stable in have not decomposed. 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 CO<sub>2</sub>.

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. Results of 12<sup>th</sup> cycle run are collected on a figure.

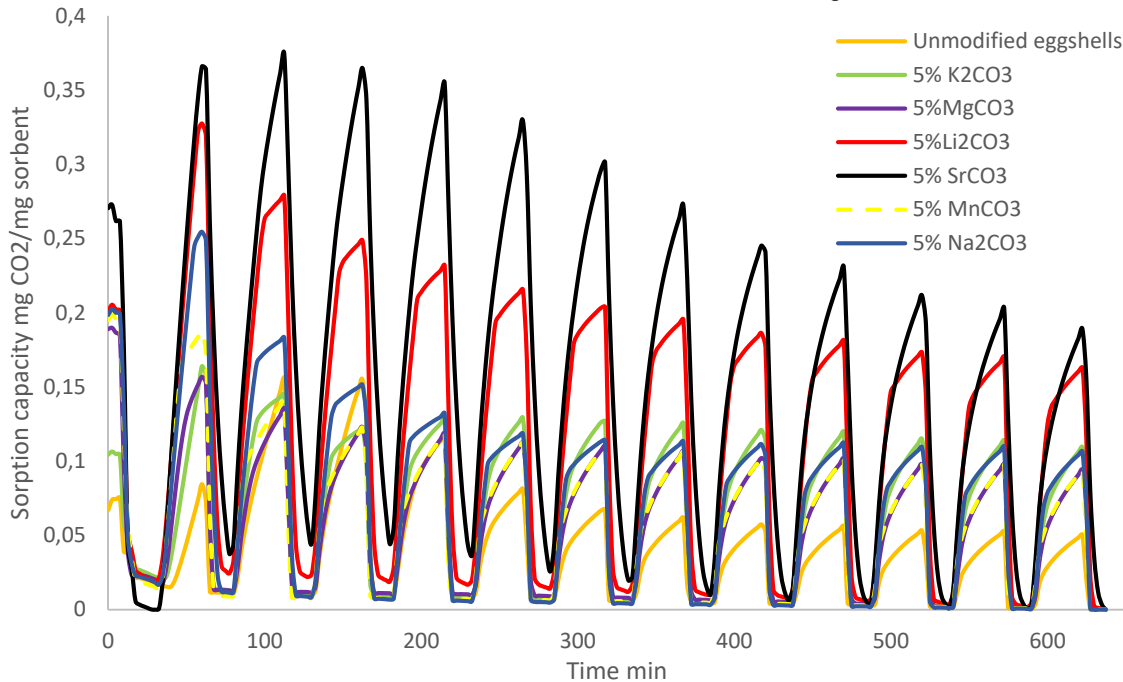


Figure 2 Thermograms of carbonate salts modified sorbent

All of the proposed have successfully increased sorption capacity throughout the whole tests. It was found out, that samples modified with SrCO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> had a good performance during the whole process, however, their sorption capacity was decreasing constantly when consecutive cycles were applied. When it comes to K<sub>2</sub>CO<sub>3</sub>, MgCO<sub>3</sub> and MnCO<sub>3</sub> modified ones, lower CO<sub>2</sub> uptake were observed at first cycles, however, after achieving specific sorption capacity results observed were constant.

As it can be seen, among all of the examined modifiers, the best influence on sorption capacity increase has strontium carbonate. CO<sub>2</sub> uptake at the first cycles is very high, equal to 0.37 mg CO<sub>2</sub>/mg sorbent. On the other hand, a significant issue is a constant decrease of

sorption capacity throughout all cycles, resulting 48% decrease when comparing 2<sup>nd</sup> and 12<sup>th</sup> 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 CO<sub>2</sub>, thus increase of carbonation time should be investigated.

When it comes to sorbent modified with Li<sub>2</sub>CO<sub>3</sub>, also reasonably high uptakes were observed, starting from 0.35 at the first cycle and ending up with 0.16 mg CO<sub>2</sub>/mg sorbent. What is distinctive for this modification, is the way how the carbonation process, looks like, after consecutive cycles, it can be noticed, that faster kinetic stage duration is constantly decreasing and the diffusional stage occurs.

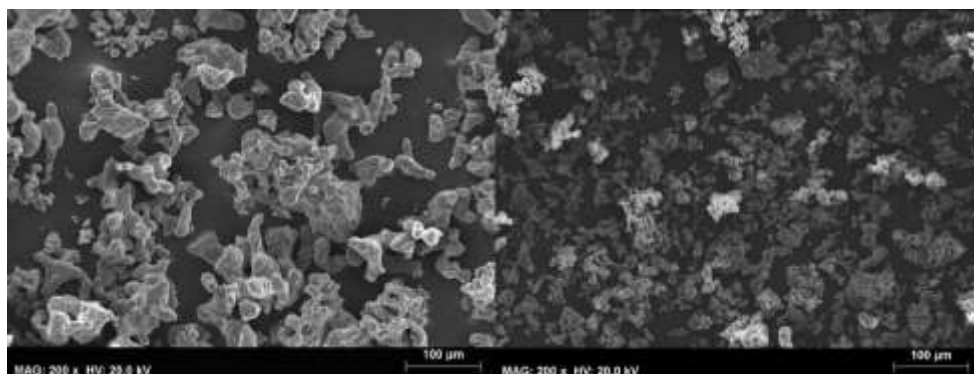


Figure 3 SEM images of  $\text{Li}_2\text{CO}_3$  (left) and  $\text{SrCO}_3$  (right) modified sorbents after longrun

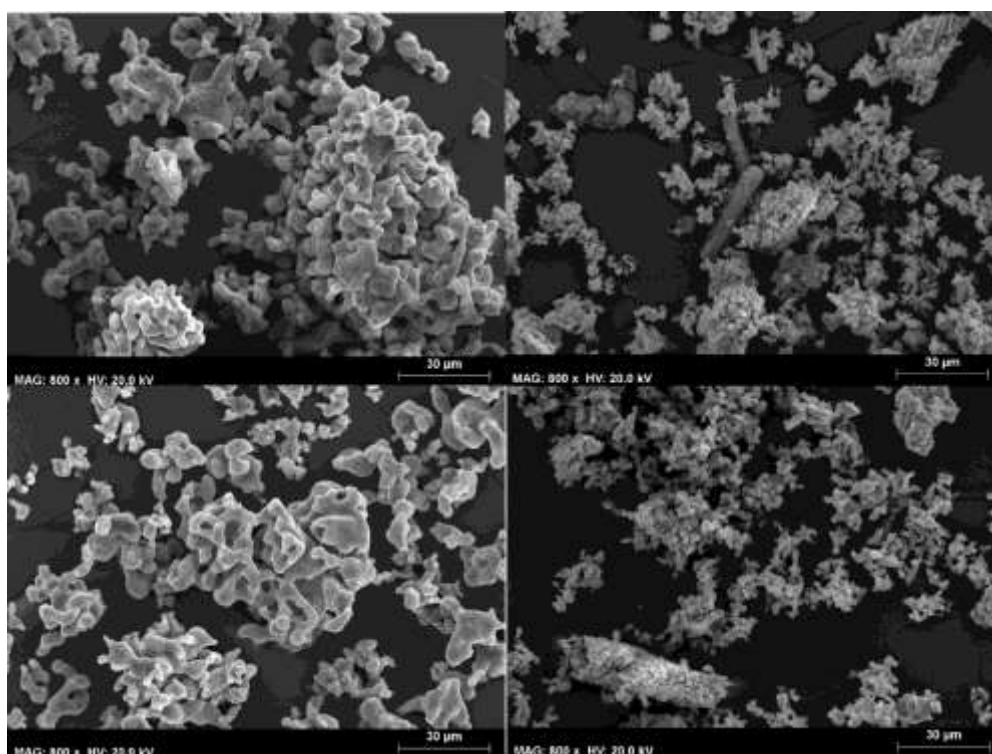


Figure 4 SEM images of  $\text{K}_2\text{CO}_3$  (left top),  $\text{MgCO}_3$  (right top),  $\text{Na}_2\text{CO}_3$  (left bottom) and  $\text{MnCO}_3$  (right bottom) modified sorbents after longrun

Comparing morphologies observed on SEM images, it can be seen, that sorbents with higher uptakes formed agglomerates with complex surfaces, what is an explanation of higher uptakes comparing to the rest of examined sorbents, which were forming bigger agglomerates with poor surface development. This is caused by attrition, which significantly affected external distribution. 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 negative effect of

sintering may lead to quick sorbent inactivation. It can be concluded, that this process may also appear on samples prepared with lithium and strontium carbonate.

### 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 Figure 5.

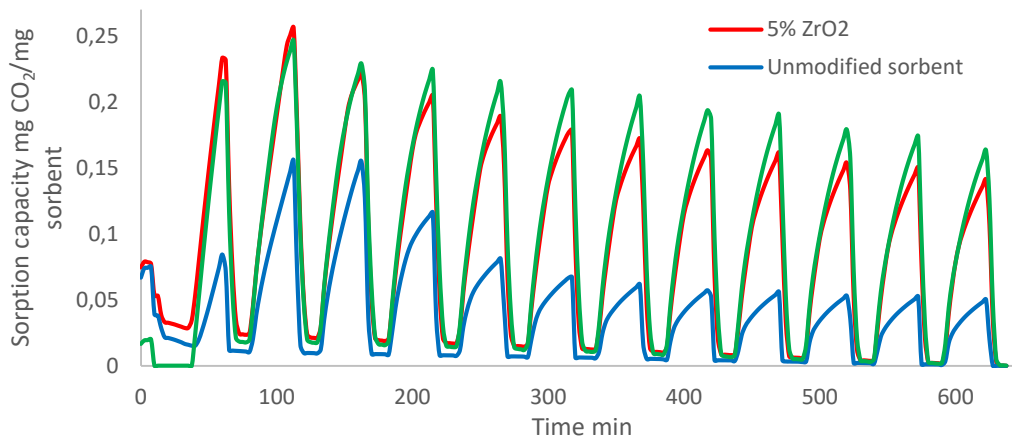


Figure 5 Thermograms for sorbents prepared by sol-gel like method after longruns

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 capacity at 1<sup>st</sup> and the 2<sup>nd</sup> cycle were bigger 3 and 2 times respectively, while at the last cycle sorption capacity for SiO<sub>2</sub> and ZrO<sub>2</sub> modified sorbents were 500 and 350% bigger.

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.

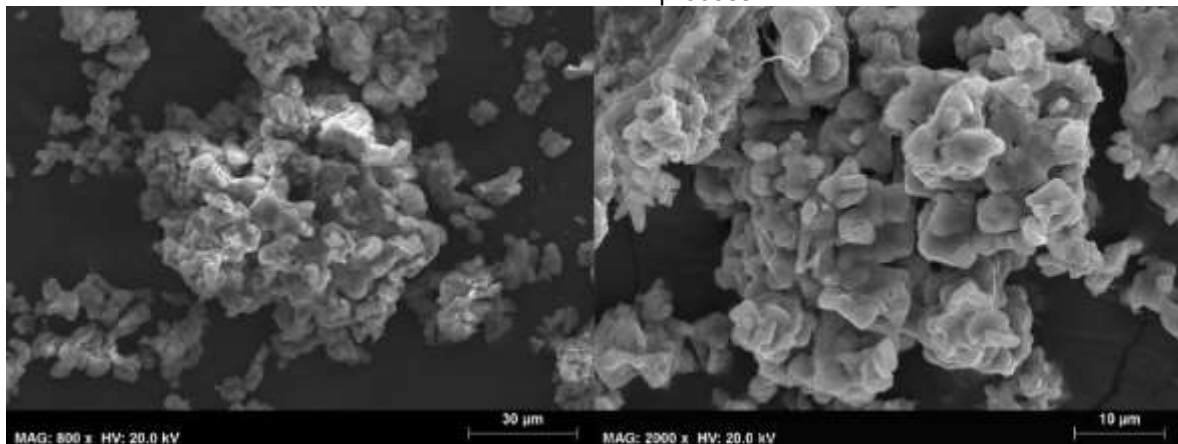


Figure 6 SEM images of ZrO<sub>2</sub> (left) and SiO<sub>2</sub> (right) modified sorbents prepared by sol-gel like method

As it can be seen on SEM images (Figure 6), 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 CO<sub>2</sub> capture.

### Influence of sorption preparation method on performance

In order to determine, which method of sorbent improvement is more suitable for increase of CO<sub>2</sub> uptake in long run experiments, two versions of silicon oxide modified sorbents were tested, one, prepared by dry mixing of SiO<sub>2</sub> with eggshells, and second, with the same reagent, prepared by sol-gel like method with addition of lactic acid. Resulting thermograms are presented on a Figure 7.

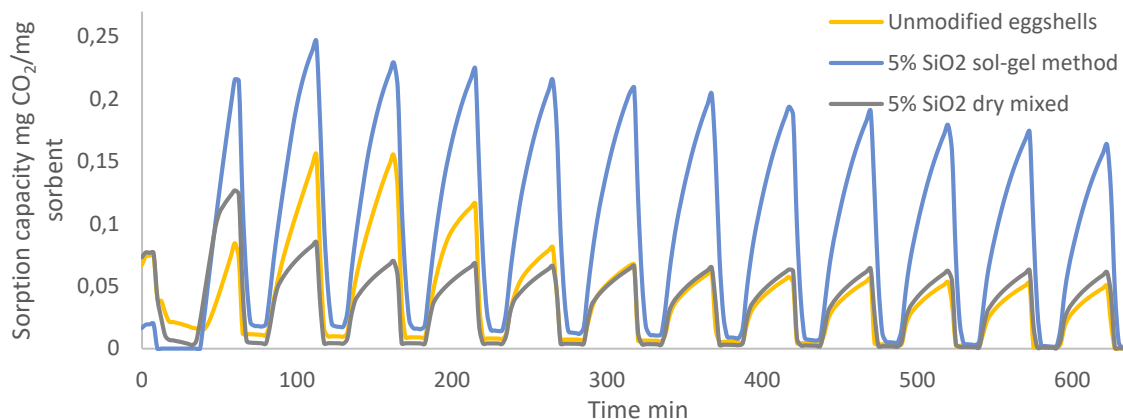


Figure 7 Thermograms of sorbents prepared by modification with SiO<sub>2</sub>

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 CO<sub>2</sub>/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 SiO<sub>2</sub> have not even increase sorption capacity at initial stages, having better results than untreated calcined eggshells from the 9<sup>th</sup> cycle and even then, the improvement was very small, 0.01 mg CO<sub>2</sub>/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 CO<sub>2</sub> capture is significantly slower.

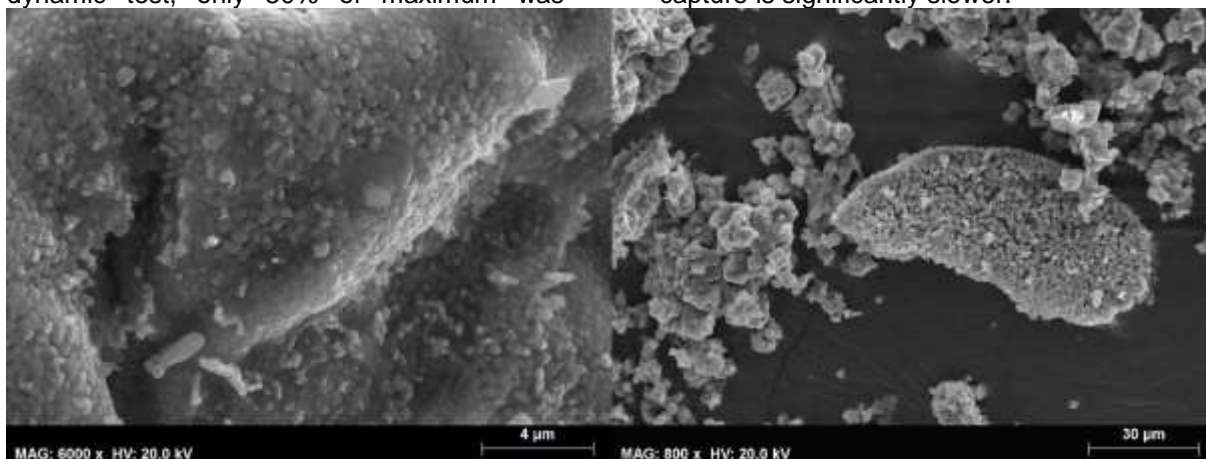


Figure 8 SEM images of dry-mixed SiO<sub>2</sub> modified sorbent (left) and using sol-gel like method (right)

As comparing morphologies on Figure 8 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 12<sup>th</sup> 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 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.

### 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 CO<sub>2</sub> 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<sub>2</sub> and second with 5% SrCO<sub>3</sub>. The first test was performed with standard conditions, while in second decarbonation time was extended to 25 minutes. Results of these comparisons are collected on Figure 9 and 10.

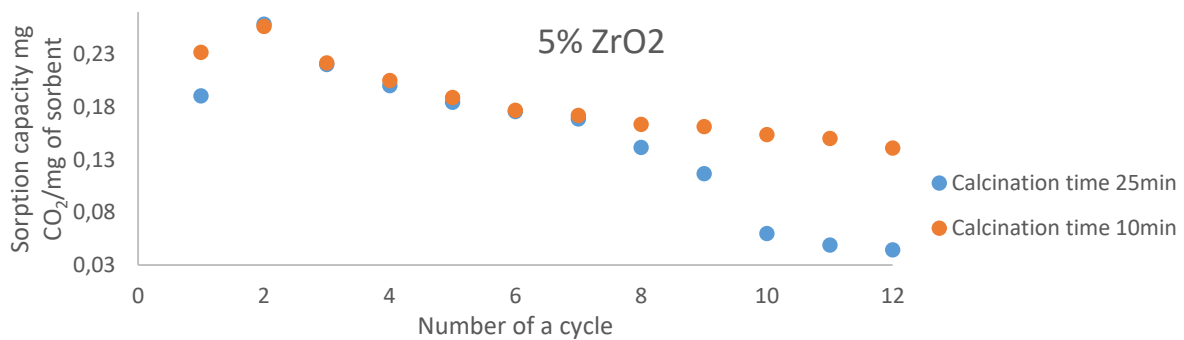


Figure 9 Evolution of sorption capacity for ZrO<sub>2</sub> modified sorbents vs. number of a cycle

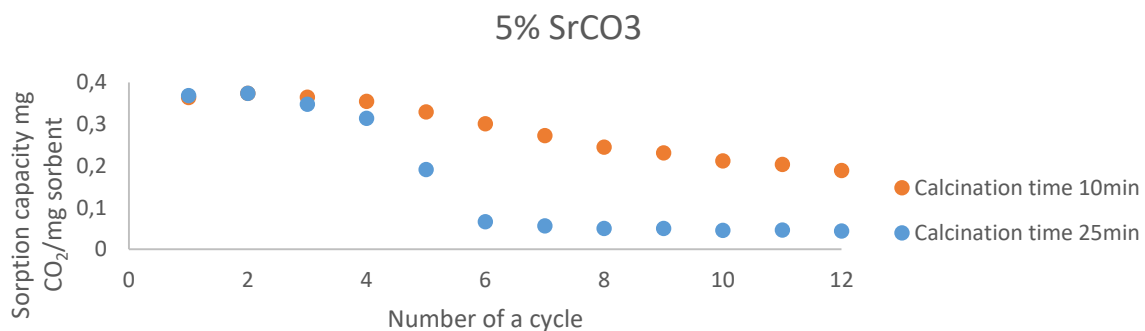


Figure 10 Evolution of sorption capacity for SrCO<sub>3</sub> modified sorbents vs. number of a cycle

For both types of sorbents decrease of CO<sub>2</sub> 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<sub>3</sub> sorbent is taken into account, where at 6<sup>th</sup> cycle decrease to 0,05 mg CO<sub>2</sub>/mg sorbent is observed. For ZrO<sub>2</sub> modified sorbent the effect of increased

decarbonation time is less drastic, where a significant drop of sorption capacity is observed during 10<sup>th</sup> cycle. this difference can be explained by different sorbent preparation method. For ZrO<sub>2</sub> 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.



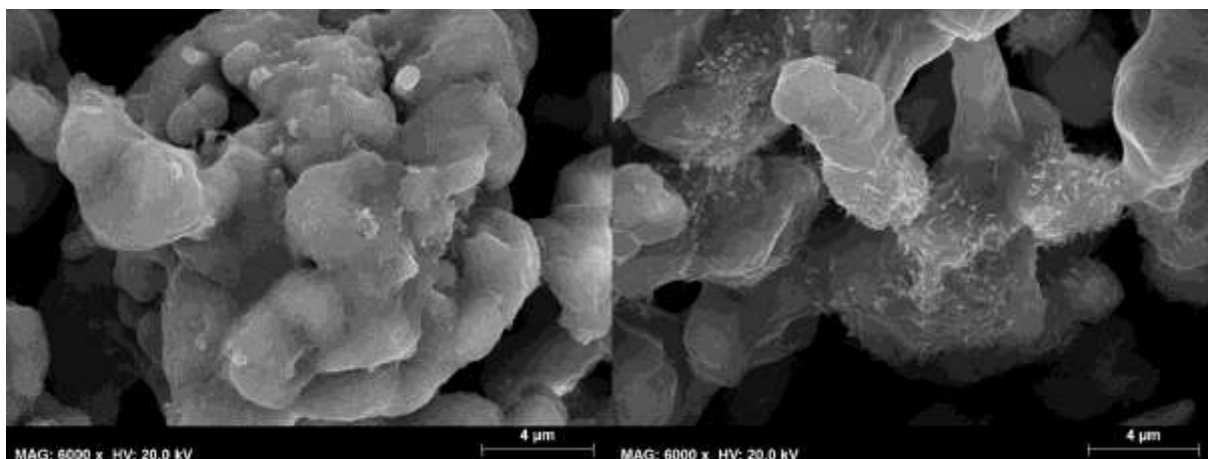


Figure 11 SEM images of  $\text{SrCO}_3$  modified sorbents after longruns (left - longer calcination time, right - shorter calcination time)

As it can be seen on SEM images of  $\text{SrCO}_3$  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  $\text{SrCO}_3$  crystals covered by  $\text{CaO}$ . 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.

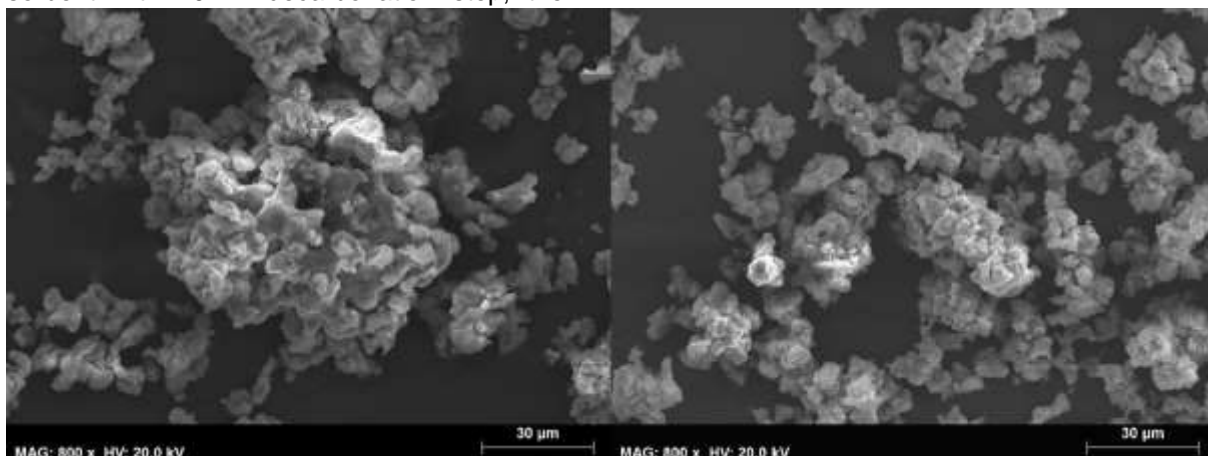


Figure 12 SEM images of  $\text{ZrO}_2$  modified sorbents after longruns (left - longer calcination time, right - shorter calcination time)

When it comes to  $\text{ZrO}_2$ , one of the main conclusions made by investigating SEM images is higher sintering of particles. Clustering in the case of longer calcination progressed to a larger extent, however, agglomerates have still the 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  $\text{CO}_2$ , decarbonation time should be

limited to an absolute minimum, in order to prevent faster surface degradation.

## Conclusions

The main goal of this thesis was to develop calcium sorbents derived from eggshells, which will be able to capture  $\text{CO}_2$ . The key properties, which were desired to obtain are satisfactory sorption capacity and decreased sorbent deactivation. 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  $\text{SrCO}_3$  and  $\text{Li}_2\text{CO}_3$  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  $\text{CO}_2$  uptake and better regenerability than samples prepared by dry mixing of feedstock and modifier.

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 later number of a cycle.

influence of  $\text{Li}_2\text{CO}_3$  and  $\text{SrCO}_3$  modification with the usage of modified Pechini route should be investigated if it allows to achieve better results. Also, interesting would be a determination of the most suitable amounts of modifiers, as well as using ones with more compounds included.

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