

CONTINUOUS TESTING OF CARBONATE LOOP IN THE FLUIDIZED BED UNIT WITH CLOSED CIRCULATION

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The study describes actual experiences with continuous testing of high temperature CO₂ sorption on limestones using a unique pilot laboratory fluidized bed reactor. The article summarizes results obtained after mathematic processing of data, collected during longer term measurements. Experiments with cyclically alternated decarbonation and carbonation phases were performed without shutting down the system. Sorption behavior of tested substrate was compared with the same parameters evaluated using two smaller-scale laboratory apparatuses. One of the laboratory apparatuses had a fixed bed reactor, while the other was equipped with quartz-made fluidized bed adsorber. The effect of different heating rates, applied in the three above mentioned apparatuses, on sample sintering of the sample was discussed and documented by appropriate SEM photos.

Keywords: carbon dioxide, limestone, fluidised bed reactor, carbonate loop.

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1. Introduction

Three studies on laboratory testing high temperature CO₂ capture onto limestone via carbonate looping were already published in the journals "Paliva" and "Zpravodaj Hnědé uhlí" during the years 2015 and 2016 [1 – 3]. In all cases the results represented partial outcomes obtained within a larger scale project, aimed at preparing complete documentation for building up an industrial scale pilot carbonate looping unit.

This work builds on the previous phases of the research and brings actual results of tests, performed using a pilot laboratory scale fluidised bed unit. Results of experiments were compared with those obtained from smaller scale laboratory apparatuses.

Currently worldwide, taking in consideration risk factors associated to global climate change, a series of methods for carbon dioxide separation from flue gas are being developed. The carbonate looping method seems to be a promising approach for post-combustion capture of this greenhouse gas. From the viewpoint of the Czech Republic good availability of various grades of limestones, representing the preferred sorbent, is an important beneficial factor for this method [4].

Based on the published reports from long term testing of pilot units it is obvious that the method is not actually developed to the state permitting its commercial utilization. The three key problems that carbonate looping technologies faces are: construction materials for the calciner, heat energy management (heat transfer optimization and improvement of efficiency) and problems with insufficient lifetime of the cyclically applied sorbent. Therefore, intensive research is still needed [5-7].

Numerous research teams deal in parallel with the last of the cited problems [8]. Different solutions were proposed to maintain the sorption capacity at the highest possible level, such as chemical reactivation [9], stabilization of CaO structure by its fixation on suitable support etc. [10, 11].

The purpose of the project, which took place at UCT Prague in the years 2015 - 2017, was, among other things, to verify crucial problematic aspects of the method of high temperature carbonate looping and to propose suitable solutions.

1.1. Aim of the study

Above all the aim of this study is to provide an overview of actual results, obtained during measurements on the above mentioned apparatus. Moreover the authors consider important to compare these results with the values, acquired using the two laboratory non-circulating flow apparatuses. The first apparatus was equipped with a fixed bed reactor, while the second had a quartz fluidised bed adsorber installed.

To make the article maximally clear the apparatuses are hereinafter marked as follows:

- pilot laboratory scale fluidised bed unit – ap. A,
- smaller laboratory fluidised bed apparatus – ap. B,
- smaller laboratory fixed bed apparatus – ap. C.

The second, but no less important, target needs to be described in more details. Measurements in all the three apparatuses were carried out at the same carbonation temperatures, under comparable gaseous atmospheres and approximately the same pressure. Regarding composition of the gaseous atmosphere, please refer to the chapter 3.1.

However, the following parameters were substantially different: volume flow rates through the sample layer, heating and cooling rates, as well as particle sizes of the samples.

As described below, variable aerodynamic and other conditions can substantially influence the sorption properties of the tested substrates. The second aim of this study is, therefore, to demonstrate the impact of these variable conditions.

2. Experimental apparatus and methods

2.1. Tested substrate

A sample base was already described in the first article, discussing preliminary results of the project. The same sample base was subsequently used for the all of the follow-up tests [1]. The sample base contained 11 different limestones, mined in the Czech Republic territory.

Based on the previously published measurements the limestone sample, mined in the quarry “Velkolom Čertovy schody”, was selected as reference sample for further comparisons within the whole project. It was the material with the highest weight fraction of CaCO_3 and the lowest contents of SiO_2 , Al_2O_3 and MgCO_3 . This substrate showed the smallest declines in the initial sorption capacity during all preliminary tests with calcinations in inert N_2 atmosphere.

As stated above, this article compares results, obtained from experiments realized independently in the three apparatuses.

Different designs of these units and especially different internal dimensions of the installed adsorbers required utilization of different particle size fractions of the sample. For better illustration the basic parameters of the experimental limestone are summarized in Tab. 1.

Tab. 1 Basic parameters of the sample (limestone “Čertovy schody”)

Parameter	Value	Unit
Apparent density	2.80	$\text{g}\cdot\text{cm}^{-3}$
Content of CaCO_3	98.86	wt. %
Content of MgCO_3	0.75	wt. %
Theoretical capacity for CO_2	43.86	$\text{g}\cdot 100\text{ g}^{-1}$
Particle sizes used in experimental apparatuses:		
Apparatus A	0.5 – 1	mm
Apparatus B	0.2 – 0.5	mm
Apparatus C	1 – 2	mm

2.2. Experimental apparatus

Capacity measurement was carried out in the self-designed pilot laboratory scale unit with fluidised bed reactor (ap. A), installed in the technological hall of the Department of Gaseous and Solid Fuels and Air Protection, UCT Prague. Schematic drawing of the

apparatus is showed in Fig. 1, although its real construction and arrangement is better visible in Fig. 2 and 3.

A vertical steel reactor with external electric heating was the fundamental part of the system. Internal diameter of the adsorber was 80 mm, where the bottom two thirds were used only for inlet gas preheating. Fluidization medium was supplied through 228 holes distributor having square network arrangement with 0.5 mm diameter of holes and 4.1 mm pitch. The entire adsorber was made of stainless steel, class AISI 316Ti.

The inlet gas was heated up using resistance furnace with input power 10.8 kW, divided into three independently adjustable zones.

Unlike the pilot units, described in other works [5-7], the overall height of the experimental apparatus A is considerably lower. The reason is as follows. The main purpose of the system was not to achieve maximum CO_2 capture efficiency, but to test the dependence of sorbent capacity changes on increasing number of sorption/desorption cycles.

Gas, leaving the adsorber, entered tangentially the filtering unit, equipped with ceramic candle filter. Regarding particle size distribution of the sample as well as volume flow rate, used for the experiments, the particle drift was relatively very small (ca 3 g). The filtering unit had an additional second function as a recuperation tubular heat exchanger. Enthalpy of the outlet gas stream was passed to the cold inlet gas, before it entered the preheating zone of the adsorber. An air cooler, followed by a safety plate water cooler, were installed after the recuperator.

Circulation of the atmosphere inside the system during closed loop regime was provided via an electric radial blower. A plastic bag was incorporated into the gas circuit in order to compensate volume changes. Volume of the gas, circulating inside the system, varies continuously due to increasing or decreasing temperature depending on the actual phase of the experiment due to corresponding chemical reactions.

Volumes of CO_2 , released into the apparatus during calcinations, or removed by the sample during subsequent carbonations, were not constant. Their value declined with the increasing number of performed cycles and corresponded with sorption capacity drop. More detailed description of this effect is given in the chapter “Results and discussion”.

Continuous measurement of CO_2 concentration inside the circulation loop of the system was realized using IR spectrometer Siemens Ultramat 23 (producer Siemens AG, Germany). The output signal was processed by the A/D converter and stored in the PC using 15 s sampling rate. The same sampling interval was applied also for recording the actual temperatures. Temperature was measured by Ni-NiCr thermocouples simultaneously at two places in the reactor axis: closely beneath the fluidization distributor and above the expanded layer of the sample.

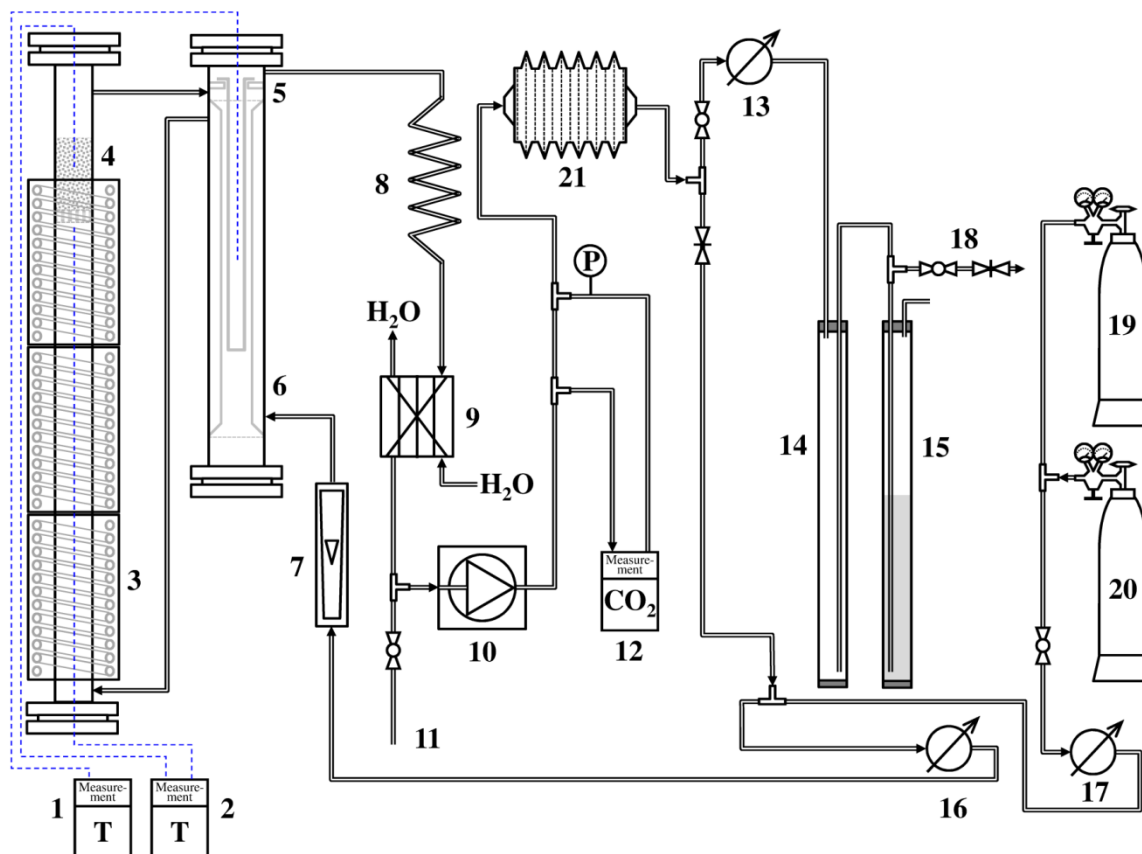


Fig. 1 Scheme of experimental apparatus (1 – thermometer / datalogger measuring temperature in the filtration column, 2 – thermometer / datalogger measuring temperature in the reactor, 3 – heating zone of the reactor, 4 – fluidised bed of sample, 5 – ceramic candle filter, 6 – recuperation heat exchanger, 7 – rotameter, 8 – air cooler, 9 – plate cooler, 10 – circulation blower, 11 – purge air inlet, 12 – IR spectrometer, 13 – membrane gas meter (for continuous flow regime), 14 – security cylinder, 15 – water manostat, 16 – membrane gas meter (for circulation mode), 17 – membrane gas meter (for gas filling), 18 – gas outlet, 19, 20 – pressure cylinders with variable filling atmospheres, 21 – compensation bag

The temperature values were processed using thermometer/datalogger Greisinger GMH 3250 with A/D converter connected to its analogue output. Continuous storing of these values was synchronized with the output of the IR spectrometer.

Gas volume flowing through the closed circulation loop of the apparatus within defined time interval was recorded manually from a diaphragm gas meter. The actual values, displayed by the gas meter, were recorded before and after each experimental phase (calcination, carbonation) and then periodically every 5 min intervals.

Because the experiments were proposed for atmospheric conditions the apparatus was equipped with a manostat, filled with isopropyl alcohol, as a safety element against overpressure.

The apparatus allowed installation of two pressure cylinders containing different gases (working atmospheres) at the same time. During the continuous measurement, hereby discussed, only inert N₂ atmosphere was chosen. The entire space of the unit was filled with N₂ before first calcination.

The photo in Fig. 4, showing the laboratory fluidised bed apparatus, allows better comparison, especially of the external dimensions of the systems.

Samples of the utilized sorbent, exposed to all sorption/desorption cycles performed either in the pilot apparatus A or in the smaller scale laboratory apparatus B, were taken after each experiment. The surface of the each sample was scanned using SEM in order to verify, whether repeated exposition to the high temperatures at the given conditions caused sintering or other structural changes of the particles. For this purpose the Field Emission Scanning Electron Microscope JEOL JSM – 7500F with cold cathode (producer JEOL Ltd., Japan) was used.

3. Results and discussion

3.1. Overall description of the course of continuous measurements

For all tests, discussed within this article and performed in the pilot laboratory scale apparatus A, 100 g of sample was used.

Measurements in this fluidised bed unit applied one parameter substantially different from the all of the already published experiments in laboratory conditions. The hereby presented unit worked always with a closed gas circulation loop.



Fig. 2 Front right view of the apparatus A
(1 – furnace controller, 2 – reactor, 3 – recuperation heat exchanger/candle filter, 4 – water plate cooler, 5 – air cooler, 6 – manometer, 7 – overpressure compensator, 8 – data collecting laptops, 9 – water flow restrictor, 10 – IR spectrometer, 11 – A/D converter, 12 – membrane gas meter with pulse encoder, 13 – pressure cylinders with gas mixtures)

Partial pressure of carbon dioxide, entering the sample layer, was therefore changing dynamically during carbonations and calcination phases of the experiment.

This experimental arrangement made possible to establish whether sorption capacity, measured with gas containing CO₂ volume fractions varying between 0 and 0.6, changed against measurements under constant CO₂ volume fraction of 0.12 or 0.14 respectively. This comparison was made using pressure higher by ca. 85 Pa than the atmospheric value (measured above fluidized sample layer). Pressure drop of the fluidizing sample varied between 350 – 380 Pa, while Δp of the distributor reached ca. 110 Pa. Gas flow rate through the blower was kept constant. Gas velocity in the adsorber was not, therefore, the same during the calcination and carbonation phases of the experiment. Depending on actual temperature it varied from 0,17 m.s⁻¹ during carbonations to the maximum value of 0,21 m.s⁻¹, when maximum calcination temperature 900 °C was reached.

The following paragraphs give detailed description of one specific test, that lasting three days and nights.

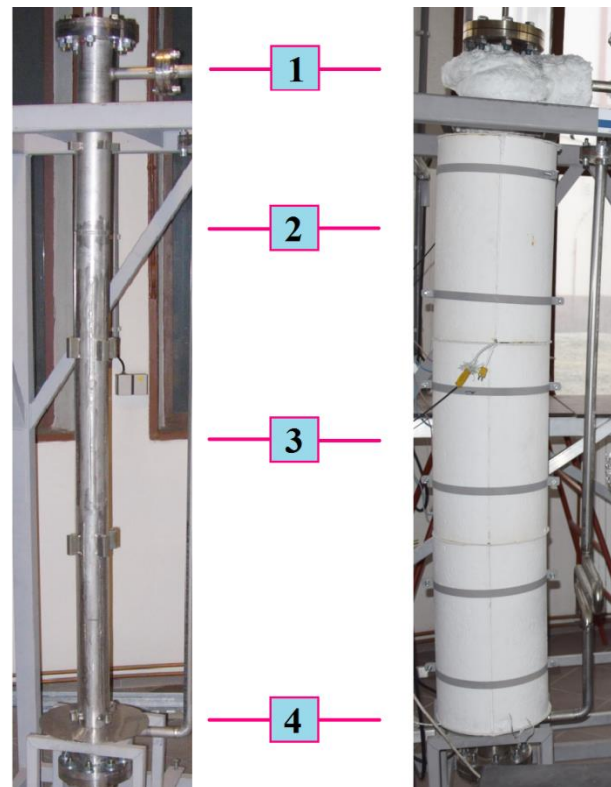


Fig. 3 Detail of the reactor (left – heating elements removed, right – three zone furnace installed, 1 – gas outlet, 2 – position of the fluidization distributor, 3 – preheating zone, 4 – gas inlet)

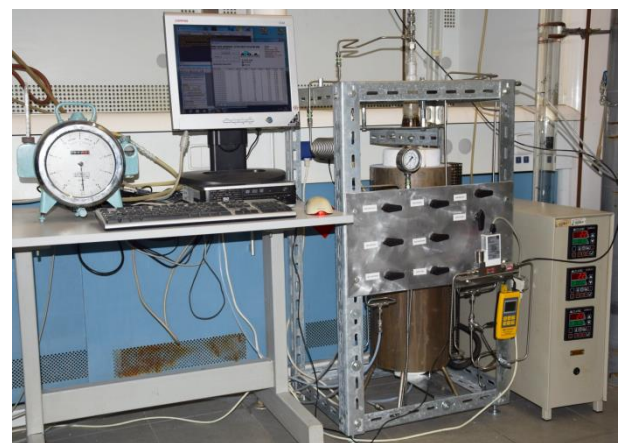


Fig. 4 Front view of the laboratory fluidised bed apparatus B

Three complete cycles of calcinations and carbonations were realized during the first day, four cycles were completed in the second day and the last three cycles were carried out in the third day. This experimental time schedule allowed to compare the sample state after exposition to an identical number of cycles as previously applied in both laboratory apparatuses B and C. The specific procedure of preparation and realization of the experiment was as follows.

The above mentioned sample weight was placed onto the fluidization distributor and the filling flange of the adsorber was closed and tightened. Before each experimental phase the test of gas tightness was provided using slight overpressure of nitrogen.

Subsequently, data acquisition from the IR spectrometer and thermometer was initialized. Immediately after this step the process continued without any interruption until the end of the entire experiment. The first phase of the measurements was calcination, when all three zones of the furnace were set to a final temperature of 900 °C applying a temperature gradient of 30 °C.min⁻¹. After reaching the required temperature on the distributor, calcination still continued under isothermal condition until desorption of CO₂ ceased.

Length of the cycles was not rigidly set as certain time interval. End of each calcination or carbonation phase was defined when 20 consecutive values of the first derivation of the curve of CO₂ concentration inside the loop was equal to zero. This was considered as a signal that the system reached equilibrium state.

Immediately after calcination terminated heating was stopped and the adsorber underwent spontaneous cooling down to a temperature of 650 °C. This temperature was confirmed by numerous measurements in the laboratory apparatuses B and C as the optimal temperature for carbonation with maximum efficacy. The cooling process started with a relatively high temperature rate of 6.5 °C.min⁻¹, which was in all experiments nearly constant until about 750 °C. The cooling rate between 750 and 650 °C was significantly slower. This effect was not caused only due to a lower temperature gradient between the furnace and the adsorber, but also due to the reaction enthalpy of the exothermic carbonation process. Therefore temperature was stabilized at the constant value of 650 °C only during the termination phase of the carbonation process. Each carbonation phase/cycle took place for approximately 120 minutes. The phase/cycle was stopped manually by the operator when recorded CO₂ concentrations signalized equilibrium as described above. Main experimental conditions, applied in the apparatuses A, B and C are summarized in Tab. 2.

Tab. 2 Fundamental conditions of experiments

Parameter	Apparatus		
	A	B	C
Max. calcination temperature [°C]	900	900 950	850 (1000)*
Heating rate for calcination [°C.min ⁻¹]	30	30	10
Gas flow rate at 23 °C [dm ³ .min ⁻¹]	16.3	1	2
Adsorber diameter [mm]	80	20	20
Input CO ₂ content for adsorption [vol. %]	Not constant	12 or 14	12 or 14

* Applied in preliminary tests, published in 2015 [2].

Another difference compared to the laboratory apparatuses B and C should be underlined. In the pilot unit A, in contrast to these apparatuses, cooling after carbonation steps did not continued till reaching ambient temperature. The system was heated up again to 900 °C and next calcination phase started instantly. This arrangement was applied for the whole experiment except during two night phases, when another property of the sample was investigated as described below.

During the night no alternation of carbonations and calcination was realized. The circulation blower was, nevertheless, kept running at stable frequency, ensuring constant flow rate inside the system. The furnace temperature was lowered during the first night. The temperature under the fluidization distributor was kept constant at 490 °C for about 10 hours. During the second night the isotherm corresponding to standard carbonation conditions i.e. 645 °C was tested instead.

There were two reasons for maintaining these isothermal conditions. The first reason was practical only. Material of the gaskets used in the reactor flanges undergoes thermal dilatation. The manufacturer did not guarantee its tightness unless the defined excessive temperature fluctuation was avoided. The second reason for maintaining the elevated temperatures during the night was due to experimental purposes. All of the previously realized experiments confirmed significant capacity decrease especially within the first five cycles. In accordance with the literature [12] the main cause for capacity loss is sintering of the sorbent particles at high temperatures. This effect should lead to closure of the porous structure of the substrate and consequently to suppression of transport of CO₂ molecules into the particles.

Based on the measurements carried out in the laboratory non-circulating flow apparatuses B and C the rate of sorption decreases gradually with increasing number of cycles. CO₂ diffusion into the calcinate should not, however, cease completely. According to the original hypothesis the sorption should continue for a long time, even though its rate would be so low and practically not usable. This effect should be manifested during the mentioned night phases by slowly decreasing CO₂ concentration in the circulating gas. Nevertheless, this hypothesis was confirmed neither in the case of 490 °C isotherm, nor at 645 °C. Together with increasing number of cycles CO₂ transport into the calcinate was not only suppressed but it ceased completely. The explanation of this behavior is discussed below in the chapter 3.3.

The evolution of the temperature closely beneath the fluidization grid and above the expanded layer of the sample is well demonstrated in Fig. 5. The graph in Fig. 6 shows, how CO₂ concentration followed the temperature program that determined the alternation of the calcination and carbonation cycles. Moreover in Fig. 6 constant CO₂ level inside the system, indicating termination of the sorption process during the night phases, can be observed.

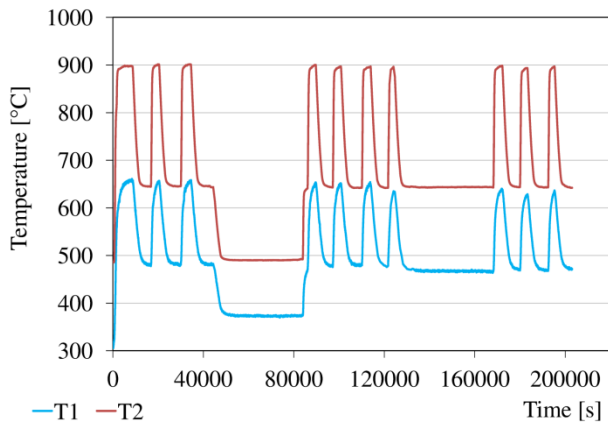


Fig. 5 Course of the two most important internal temperatures during continuous tests (*T1* - temperature above the fluidised sample layer, *T2* - temperature at the distributor)

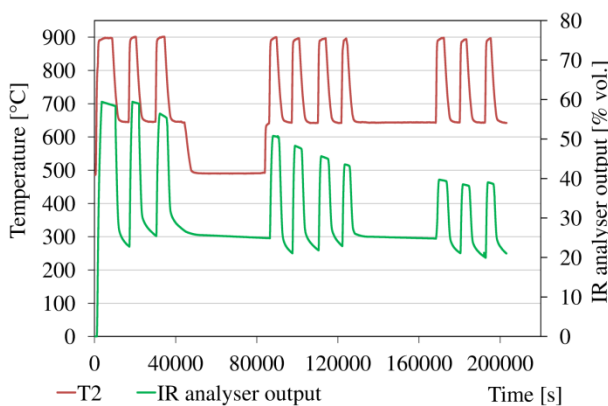


Fig. 6 Dependence of CO₂ concentration inside the apparatus A on the actual temperature (*T2* - temperature at the distributor)

3.2. Capacity changes observed at different experimental conditions

Correct evaluation of sorption capacity is essential for the overall assessing of the process of cyclically repeated sorption and desorption. Evaluation of this parameter was provided on the basis of recorded data regarding immediate CO₂ concentration in the system and volume gas flow in the circulation loop. A graph, where the values of the membrane gas meter were put against the time scale, showed that the circulation blower with the frequency converter was able to maintain the gas flow constant throughout the whole three day experiment.

Due to the flexible bag, installed in the circulation loop, all volume changes of the gas during individual phases of the experiments were compensated and atmospheric pressure was therefore maintained constantly.

The following parameters were calculated for each experimental cycle. Weight of carbon dioxide, released into the inner space of the apparatus due to thermal decomposition of the sample, was calculated for the

calcination phases. Weight of CO₂, captured from the circulating atmosphere by the calcined sample, was expressed for the carbonation steps.

In general terms it can be said that the same mathematic approach was also used for the both laboratory apparatuses with no-circulating gas flow. Weights of captured as well as desorbed carbon dioxide can be therefore mutually compared without needing any additional mathematic correction.

For better clarity all results, showing adsorbed or desorbed amount of CO₂, were expressed for 100 g of the initial dry sample/sorbent before its first calcination. Changes in the values of adsorbed and desorbed CO₂, processed by the previously mentioned mathematical approach are shown in Fig. 7. The graph contains also data, obtained during experiments in the laboratory fluidized bed apparatus B.

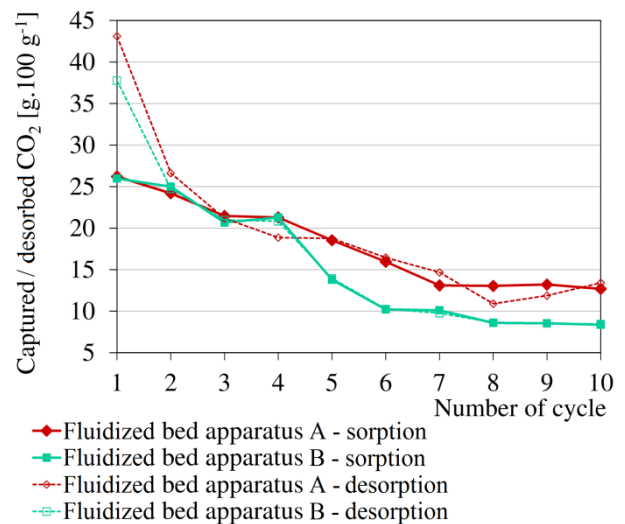


Fig. 7 Comparison of adsorbed and desorbed quantities of CO₂, expressed for pilot and laboratory fluidised bed apparatuses A and B

Based on the course of ten cycles, carried out independently in the two apparatuses the following information can be derived. Measurements in the semi-industrial fluidized bed apparatus confirmed the findings from the laboratory tests. Structural changes, causing gradual decrease in sorption capacity, occur already during the first calcination. This fact can be documented by the great difference between the weight of CO₂, desorbed during the first calcination, and the weight of CO₂ captured back during the subsequent (second) carbonation.

Sorption capacity continues to decrease significantly. However, after the seventh or eighth cycle the rate of this decline slows down substantially. Besides these corresponding results several differences in sorption behavior were observed when comparing the apparatuses A, B and C. These findings demonstrate how different construction and geometry of the experimental

devices and therefore slightly different thermodynamic conditions influence the samples and their capacities.

The course of the sorption capacities is in fact the same until the fourth cycle regardless of the apparatus design. In this cycle the sorption capacity of the sample was $21.3 \text{ g} \cdot 100 \text{ g}^{-1}$ for the both fluidized bed apparatuses A and B.

After that in the apparatus A the capacity decreased more or less linearly until the seventh cycle, when the capacity stabilized at the value of ca $13 \text{ g} \cdot 100 \text{ g}^{-1}$. On the other hand, in the laboratory apparatus B significant decline in capacities was detected also in the fifth and sixth cycle. Since the eighth cycle the capacity was roughly stabilized and its value was about $8.5 \text{ g} \cdot 100 \text{ g}^{-1}$, which means a difference of $4.5 \text{ g} \cdot 100 \text{ g}^{-1}$ compared to the larger apparatus A.

The causes of this behavior can be explained by two factors. Maximum calcination temperature was the first parameter. During tests in the all three apparatuses calcination temperatures in the range of $850 - 1000 \text{ }^\circ\text{C}$ were applied. The highest number of experiments with various settings of the maximum calcination temperature was realized in the fixed bed laboratory apparatus C.

The temperature of $850 \text{ }^\circ\text{C}$ was repeatedly confirmed as the minimum temperature, necessary for complete decomposition of any CaCO_3 based sample. From the viewpoint of structural changes this temperature was chosen as the most suitable. On the other hand this setting substantially prolonged calcination time. The temperature of $1000 \text{ }^\circ\text{C}$ leads to practically immediate conversion of CaCO_3 to CaO . However due to a series of reasons, such as stability of construction materials, this temperature is not applicable for industrial practice.

In the fluidised bed laboratory apparatus B the maximum calcination temperature of $950 \text{ }^\circ\text{C}$ was tested in order to insure fast decarbonation of the sample. Because the semi-industrial unit had the adsorber made of stainless steel AISI 316Ti, maximum calcination temperature $900 \text{ }^\circ\text{C}$ was chosen as a compromise. Anyway, $50 \text{ }^\circ\text{C}$ of difference in calcination seems to be the key factor causing the different trend in the reached sorption capacities.

The second factor was significantly higher partial pressure of CO_2 in the gas, circulating in the apparatus A. Both laboratory apparatuses B and C worked always with gas mixtures with defined composition and containing CO_2 in the range of $12 - 14 \text{ vol. } \%$. While in the closed circulation of the pilot laboratory scale apparatus A the content of CO_2 , detected at the end of the first two calcinations, reached up to $60 \text{ vol. } \%$. Until now the of partial pressure of CO_2 on sorption capacity has not been experimentally quantified and will be therefore investigated in future measurements. This effect was, however, discussed in several literary sources/scientific publications [13].

3.3. Effect of steam and SO_2

It is useful to put the capacities of the tested limestone into the context with another two factors, whose impact was already documented during the laboratory experiments. It is specifically the effect of steam reactivation and the effect of low concentration of SO_2 in the simulated flue gas. Both effects were already published [1, 2], but the results were not yet compared with the apparatus A. The graph in Fig. 8 depicts mutual comparison of the effect of the above mentioned factors on sorption capacities.

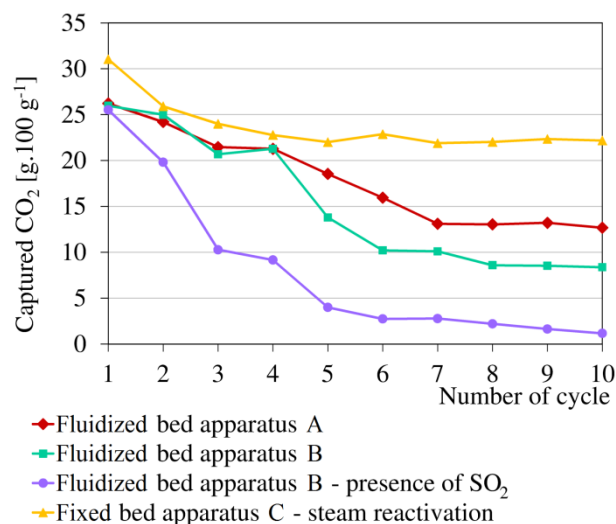


Fig. 8 Comparison of sorption capacities, realized on different apparatuses under variable experimental conditions

Assuming that the economical assessment of carbonate looping process shows that sorbent capacities in range $9 - 12 \text{ g} \cdot 100 \text{ g}^{-1}$ will be sufficient it is nevertheless possible to maintain sorption capacity more or less stable by optimizing the temperature regime even without applying any additional reactivation step. Taking in consideration that the effect of steam reactivation and the influence of sulphur dioxide in the gas stream have already been discussed in previous works, this work does not address these issues.

3.4. Structural changes of the sorbent particles

SEM photos document very illustratively the reason why the above described changes in sorption capacity occur once the sorbent has been subjected to periodically alternating phases of carbonations and high temperature calcinations.

By the comparison of amounts of CO_2 adsorbed and desorbed in each cycle following assumption can be expressed. As seen in Fig. 7 the declines in sorption capacities occur due to both incomplete release of CO_2 during calcinations as well as its incomplete capture during carbonation phases. It is probable that these phenomena are caused by structural changes blocking

CO₂ molecules transport out or inside the sorbent particles.

Above all, SEM photos explain why CO₂ transport into the calcined sorbent stopped and sorption terminated completely during prolonged circulation under isothermal conditions at 650 °C.

As seen in Fig. 9 and 10, the surface of the material is practically free of pores. Only a network of cracks, caused by thermal dilatations and contractions, can be observed on the relief. This is especially noticeable when magnification 5×10^4 was used for scanning. The surface of the individual grains, forming the agglomerate, appears smooth and intact and therefore significantly prevented diffusion of CO₂ molecules. During the next cycle new fissures are formed, thus again enabling the carbonation process, although with lower conversion rate.

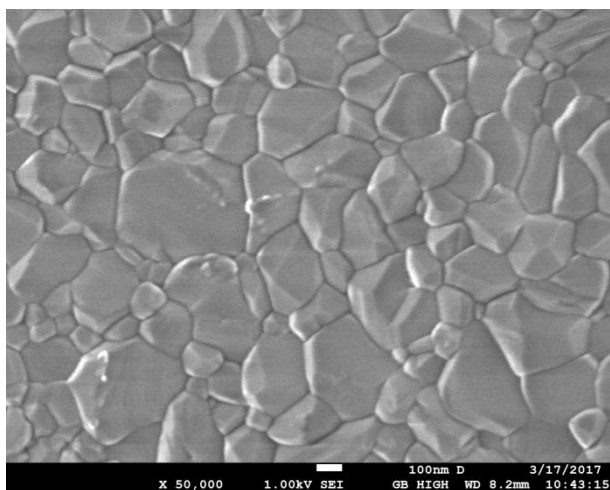


Fig. 9 Surface of the sample after ten cycles of high temperature calcination, followed by carbonations (magnification 50000)

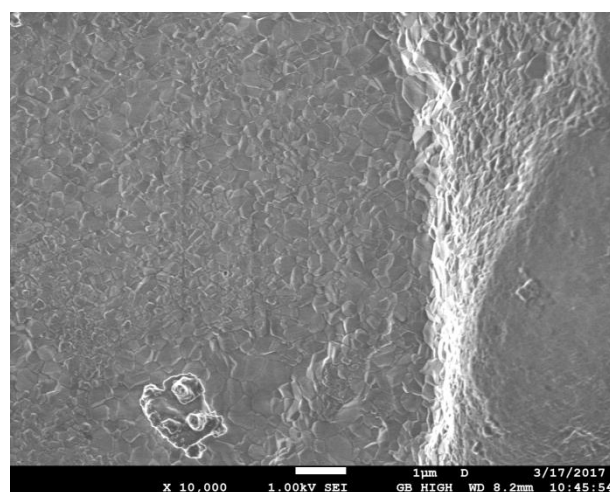


Fig. 10 Surface of the sample after ten cycles of high temperature calcination, followed by carbonations (magnification 10000)

This finding is supported by several literature sources, as well as the parameters of CO₂ molecule, which has its kinetic diameter 330 pm for O=C=O bonding angle of 180° and C=O bond length 1.16×10^{-10} m [14, 15].

The same phenomenon was observed during experiments in both laboratory apparatuses B and C. In this case one difference was found.

If calcination was performed in the apparatus C process of surface sintering occurred somewhat slower. Significantly lower heating rate, applied for calcination, was identified as the reason for this behavior.

4. Conclusion

This work compares results of the sorption experiments performed in parallel in three different apparatuses. Function and features of the pilot laboratory scale unit with fluidized bed reactor and closed gas circulation are established by performing a specific three-day experiment as an example. Method of processing the collected data is discussed as well.

All experiments fully confirmed the findings of measurements in smaller apparatuses B and C. All the measurements showed that CO₂ sorption capacity of limestones is more or less stabilized after the first six or seven cycles. The specific value for the tested sample after stabilization varies in the range of 9 – 12 g. 100 g⁻¹. It seems that shift of the stabilized sorption capacity to lower or higher limit within the interval depends strongly on temperature conditions in the calciner (temperature profile and heating rate).

Night phases of prolonged carbonation under isothermal conditions confirmed that closure of the porous structure leads not only to a decrease of carbonation rate but to practically complete stop of adsorption.

It should be noted that the purpose of the pilot laboratory scale unit A was not reaching high efficiency of CO₂ capture but providing data about sorption capacities and their changes. Due to economic reasons, in the case of industrial application of carbonate looping the number of calcination/carbonation cycles should reach tens or better hundreds of repetitions for one limestone batch. Based on the above described measurements it is obvious that this arrangement excludes confronting the calcinate with insufficiently desulphurised flue gas.

Alternatively, carbonate looping can be used for single step combination of dry FGD and CO₂ capture. In that case the performance of regeneration and number of cycles would be, however, significantly limited.

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Summary

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Continuous testing of carbonate loop in the fluidized bed unit with closed circulation

The article summarizes results of measurements of the equilibrium sorption capacities of natural limestone, obtained using a carbonate looping unit with pilot laboratory scale.

One material, mined in the quarry “Velkolom Čertovy schody”, was selected on the basis of previously performed preliminary tests under laboratory conditions. The selected sorbent material was subjected to the hereby presented cyclical measurements.

The paper contains detailed description of the experimental device, having a single fluidized bed reactor, which plays both the roles of the calciner and the carbonator as well. A three-day experiment was used as an example to demonstrate the arrangement of the tests and their evaluation.

Unlike the devices with separated reaction chambers for sorption and desorption the apparatus, constructed for the hereby discussed experiments, allowed changing the process phases simply by controlling/setting the temperature of the external three-zone oven. In all cases the gas flow rate was maintained constant at 16.3 dm³.min⁻¹ (blower temperature 23 °C).

The final temperature for the calcination phase, measured on the fluidization distributor, was set at 900 °C, while carbonation was carried out at isothermal conditions at 650 °C.

Within the article the values of the achieved capacities and their changes, depending on the number of exposition cycles, are compared with the corresponding data from two smaller laboratory non-circulating flow apparatuses. The first of the comparative apparatuses worked with fixed sample/sorbent bed, while the second system was operated with fluidised bed.

Close relation between sustainable capacity and calcination conditions was confirmed. Depending on the

maximum calcination temperature and heating rate the capture capacity of the given limestone can be more or less stabilized in the range of 9 - 12 g.100 g⁻¹. The SEM photos, taken after 10 cycles, showed how the high calcination temperatures influenced the particles surface and determined the available sorption capacity of the sample.