

Evaluation of natural limestones quarried in the Czech Republic in terms of their use in carbonate looping

Marek Staf¹, Karel Ciahotný¹ and Tomáš Hlinčík¹

For effective operation of high-temperature sorption of carbon dioxide from the flue gas in industrial scale, it is necessary to ensure an adequate supply of affordable sorbent having suitable technical parameters. For a given technology, natural limestones meet the condition of low cost. Due to current needs to solve the issue of carbon dioxide capture in power as well as other branches of industry, this study is focused on evaluating different types of natural limestones. A set of laboratory methods for evaluation of the physicochemical properties of limestones was proposed. A laboratory apparatus, based on the principle of fixed bed tubular reactor made of quartz glass, represented the main method for measurement sorption capacities. Within the sample base, a wide spread of sorption capacities was determined in the range of 18.0 - 84.6 % of the theoretical values, based on chemical composition. After six cycles the sorption capacity decreased to 3.5 - 35.6 %, compared to the theoretical value, mainly due to sintering. It was verified that appropriate selection of limestone can significantly reduce degradation of the capacity during cyclic use.

Key words: Limestone; Carbon dioxide; Sorption; Carbonate looping; Post-combustion capture.

Introduction

The initiative in searching for technologies that would contribute to solving the global climatic changes started in the relatively recent past. In the early 1970s, the hypothesis was first published, which suggested that CO₂ is the main anthropogenic greenhouse gas. Later, in the mid-1970s, studies were published about other greenhouse gasses, mainly CFCs, etc. People became more widely aware of the issue of greenhouse gases thanks to a 1985 report by the World Meteorological Organization (WMO). The cooperation between WMO and the United Nations Environment Programme (UNEP) led in 1988 to the foundation of the Intergovernmental Panel for Climate Change (IPCC). IPCC First Assessment Report in the new millennium from 2001 confirmed the original predictions made in the 1980s and revealed that the global mean temperature between 1900 and 2005 increased by 0.8 °C. In 2007, the original estimates were refined, suggesting that about 30 % of global warming can be attributed to natural causes, while the remaining 70 % is anthropogenic. Currently, the proportion of sceptical views to views corresponding with the findings of IPCC tends significantly to the latter as pointed by Ramanathan and Feng (2009).

As regards the reduction of CO₂ emissions into the atmosphere that would not at the same time lead to a decrease in industrial production and power production efficiency, there are, as stated by, for example, Figueroa (2008), four ways available. These are: reducing the use of carbonaceous fuels, increasing the efficiency of energy production in the existing sources, developing new energy sources, and developing economically acceptable technologies for CO₂ capture.

The research presented here is concerned with the last of the ways mentioned above. Carbonate looping has been studied in recent years within a wider group of methods called chemical looping, which summarised Gomes (2013). The principle is based on the chemical reaction of gaseous carbon dioxide at elevated temperature with a suitable oxide (e.g. calcium oxide), producing carbonate. The process is made reversible by increasing the temperature above the limit of thermal stability of the carbonate, which ensures prolonged cyclical use of the initial batch of sorbent. Materials suitable for use in carbonate looping were listed in, for example, the study of Manovic and Anthony (2009). These materials can be natural, such as limestones, which are tested here, as well as synthetically produced from suitable precursors.

One of the primarily considered possibilities of applying high-temperature carbonate looping on an industrial scale is incorporating this cycle as a post combustion method for removing carbon dioxide from flue gas from fossil fuel combustors (e.g. in coal power plants). Fig. 1 schematically shows the general principle of high-temperature carbonate looping.

A similar mechanism, described by Alonso et al. (2014), was designed for, for example, on site CO₂ capture in biomass combustion, or for CO₂ separation during hydrogen production using methane steam reforming, which method was studied by Yong et al. (2001).

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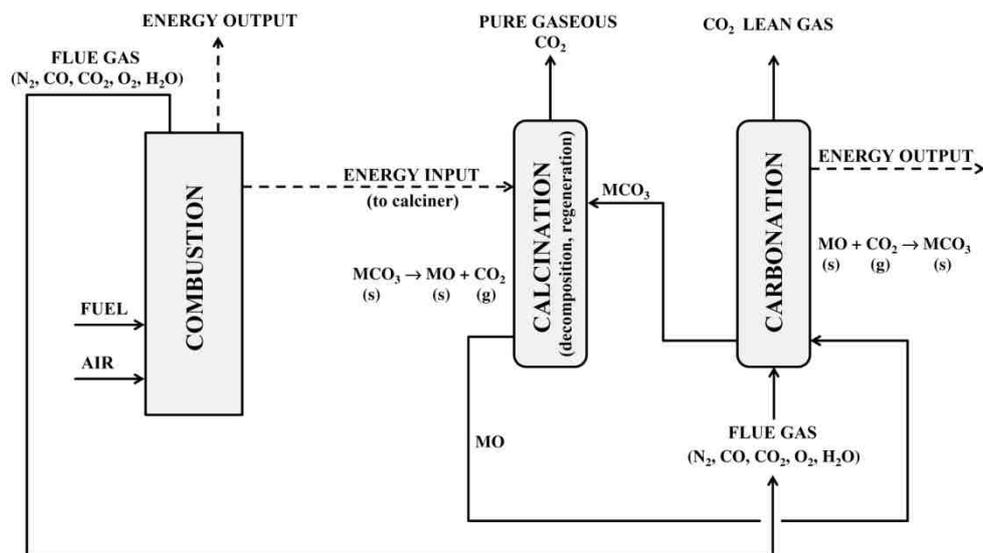


Fig. 1. General scheme of carbonate looping (Staf, 2016).

A number of methods have been elaborated for capturing carbon dioxide on various types of solid sorbents. A great deal of attention has been paid mainly to sorbents containing CaO. Promising properties, however, described Oliveira et al. (2008) in materials based on synthetic hydrotalcite, or Fauth et al. (2005) in sorbents based on Li_2ZrO_3 etc. If a sorbent is to be successful in practice, it should fulfil certain general criteria. Ideally, a sorbent used for CO_2 capture on an industrial scale should have the following characteristics:

- High sorption capacity emphasised by Herzog et al. (1997).
- Ready availability and low acquisition costs.
- Selective CO_2 sorption with resistance to contamination by other flue gas components as mentioned by Fauth et al. (2005).
- The ability to sorb CO_2 in the wide range of its partial pressures.
- Good kinetics of the sorption and recovery process mentioned by, for example, Ruether (1999).
- Low energy complete recovery by changing temperature or pressure.
- The ability to sorb CO_2 at high temperatures.
- The Minimal decrease in sorption capacity during multi cycle sorption and recovery emphasised by, for example, Dave et al. (1999).
- Sufficient mechanical strength and abrasion resistance, studied by Burchell et al. (1997).

Currently, known sorbents still show some deficiencies that hinder their effective application in commercially viable technology. There are many studies exploring the possibilities of removing those deficiencies. The possibilities in general are summarised e.g. by Huang et al. (2010), who lists the main directions of CaO sorbent research. The basic current research activities are as follows:

- Chemical pretreatment of natural sorbents, published by Manovic et al. (2008).
- Preparing new synthetic sorbents, studied by, for example, Gupta and Fan (2002).
- Testing the impact of different precursors on the characteristics of the final sorbent, published by, for example, Lu et al. (2006).
- Introducing dopants (e.g. through impregnation) into an existing sorbent, tested in laboratory scale by Hong et al. (2009).
- Incorporating inert substances to increase the stability of sorbent structure also tested in laboratory scale by Martavaltzi et al. (2010).
- Hydrating CaO sorbents by steam, verified both in the laboratory as well as semi-industrial scale as described by Manovic and Anthony (2007).

The above methods, however, bring about additional financial costs, namely the price of sorbent production or its chemical modification.

Several less expensive methods have been investigated, for example, in Poland. In order to eliminate undesired capacity drop, Kotyczka-Morańska and Tomaszewicz (2014) proposed two treatments of the raw limestone. As the first method, the authors examined washing the material with a diluted hydrochloric acid. The second method used ultrasound waves, generating subsequently imploding microscopic bubbles filled with water vapour or gas inside the sorbent particles. Both procedures should diminish the formation of sintered areas

in the calcinate. Treatment using hydrochloric acid lead to chlorine salts that did not perform the function of a framework in modified sorbents. Contrariwise the reactivation with ultrasounds enhanced the limestone activity, which makes this method more promising. Improvement of sorption properties was not, however, sufficient so the method requires further development. Within a subsequent research, Tomaszewicz et al. (2016) verified positive impact of increased CO₂ partial pressure on the both sorption capacity and the process kinetics. In the both studies measurements of carbonations/decarbonations were carried out by means of thermogravimetric analysis.

The research presented here focuses on the issue of effective use of natural materials which have the deficiency of decreased sorption capacity as a result of cyclical use, but whose great advantage is their ready availability and low acquisition costs.

In fact, implementation of any CO₂ capturing system causes extra costs of a sorbent regeneration. The penalty depends on the overall enthalpy balance of the process. In the case of chemical sorption onto CaCO₃-based materials, the balance of calcination includes: heat to increase the temperature of the sorbent up to calcination level (ca. 1170 K) and a reaction enthalpy of endothermic decomposition of CaCO₃, which value 178.2 kJ.mol⁻¹ was used for process calculations by, for example, Li et al. (2010). Depending on a calciner and carbonator construction, a part of the energy can be recovered in a waste heat boiler. Romano et al. (2013) wrote that Ca-looping implementation on a reference coal-fired power plant of 46 % electric production efficiency leads to efficiency penalties in the range between 6.5 and 8.5 percentage points. From these values, approximately 3 percentage points, however, attributed to the compressor and the air separation unit. The exact value depends especially on a level of waste heat utilisation. For this estimation, the authors compiled outcomes of mathematic models and process data from several pilot scale units.

The aims of the presented research

The research presented here is part of a more extensive research, the aim of which is to create a draft concept of a pilot unit for studying flue gas decarbonisation using high-temperature looping, and subsequent documentation for constructing a semi-industrial unit for testing the use of this looping process in practice.

The specific outcomes of this partial research are as follows. The primary objective was to identify the limestones which are suitable for further testing on a semi-industrial unit and which are expected in future to be used in an industrial pilot plant. This primary aim was achieved by obtaining a set of numerical and graphical data about sorption capacities from isothermal measurements of breakthrough curves. The experimental values provided the basis for an overview of the realistically achievable sorption capacities which limestones from the individual deposits can offer. Testing in practice verified the optimal carbonisation temperature at which carbonation reactions have good kinetics. A secondary aim of the study was to assess the limestones in terms of the decrease of their sorption capacity due to the structural changes which, according to works published earlier by, for example, Feng et al. (2006), occur during cyclical alternation of the processes of calcination and carbonation. The problem of high-temperature sintering, which reduces the reversibility of the reaction $\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2$, was pointed out more than forty years ago by Barker (1973).

Experimental

Sample base

Samples of natural limestones from 11 quarries located across the Czech Republic were acquired for the realisation of this study. The localities of sampling and the individual samples were selected so that they would cover an as large area of the Czech Republic as possible, and that the scale of calcite content in the samples included in the sample base would be as wide as possible. A complete list of samples and the respective quarries is given in Table 1, which also summarises the basic physicochemical characteristics of the samples. Selected geological data about each sample were also collected for practical reasons, namely quarry stage and blast date identification, but these values are not significant for the purposes of the study presented here. Each limestone in the sample base was provided in quantity from 150 to 200 kg and was declared as representative for the whole exploited seam by the geologist of the corresponding mining company. Laboratory samples for analyses were prepared by quartering from the mentioned stored weight.

In the first phase of the research, which is the subject of this contribution, the samples were not chemically modified in any way.

Before the commencement of the testing of the materials in terms of carbon dioxide sorption, the samples were subjected to X-ray fluorescence analysis (XRF) to determine their elemental composition. The course of calcination of small sample amounts was mapped by means of thermogravimetric analysis (TG).

XRF analysis was conducted on ARL 9400 XP+ apparatus using evaluation program UniQuant. Five monochromators and their combinations with a flow or scintillation detector were used for the measurements. The determined elements were divided into five groups from light to heavy, and each group was assigned individual excitation voltage ranging from 30 kV/80 mA to 60 kV/40 mA. The results were normalised for

100 % weight and expressed as oxides, with CaO and MgO being subsequently converted to carbonates by the software.

TG analysis was carried out on Navas Instruments TGA 2000 apparatus. The measurements included only calcination, up to a final temperature of 1273 K. Unbound water was determined by heating the sample to 378 K at the speed of $12 \text{ K}\cdot\text{min}^{-1}$, with a subsequent isothermal delay to achieve a constant weight. This was followed by heating at $5 \text{ K}\cdot\text{min}^{-1}$ to the final calcination temperature of 1273 K. Furnace cooling was initiated after the final temperature was reached, with no isothermal delay. Sample crucibles were fitted with lids through the entire temperature range. The analysis was carried out in a nitrogen atmosphere.

Sample intakes for the purposes of measuring sorption capacities and for providing supporting analyses were obtained by quartering and subsequent vibratory sieving of a large weight (50 kg) of raw material, crushed by an engine powered jaw mill.

Experimental apparatus

Sorption capacities of the samples were determined using a laboratory apparatus of own construction, the scheme of which is shown in Fig. 2 and a photograph of the actual apparatus in Fig. 3. The testing proceeded under dynamic conditions in a flow quartz reactor with fixed sample bed. The reactor was placed in a vertical cylindrical furnace standing on a scissor lift platform, which enabled the reactor to be quickly pulled out, thus making it easier to cool down the apparatus when changing the temperature regime of the experiment. Gaseous media were fed into the apparatus through stainless steel capillary tubes from a pair of pressure bottles. The gas flow rate was regulated by digital mass flow meter Bronkhorst EL FLOW Select coupled to an electromagnetic regulator. The gas was fed to the base of the reactor, and after passing through a layer of inert material providing preheating and even distribution over the cross-section of the reactor, it passed through a layer of loose fill sample. The temperature of the layer of the sample was continuously measured by a Ni CrNi thermocouple lead in the axis of the reactor and recorded by digital thermometer/datalogger Greisinger GMH 3250. The gas exiting the reactor was cooled in several spiral air coolers connected in series. Another mass flow meter Bronkhorst was connected at the outlet of the reactor after the coolers, and its purpose was to continuously record data about flow rate and thus check the accuracy of regulation. The analysis of gas at the outlet of the reactor was carried out by infrared spectrometre ASEKO AIR LF. Measuring initial CO_2 content in the feeding gas and calibrating the IR analyser was possible thanks to a bypass, by means of which it was possible to feed the gas directly to the analyser, without it coming into contact with the sample. Because the correct measurement of the volume of gas that passes through a layer of the sample is a vital prerequisite of a correct evaluation of sorption capacity, a wet drum gas meter was connected to the end of the apparatus.

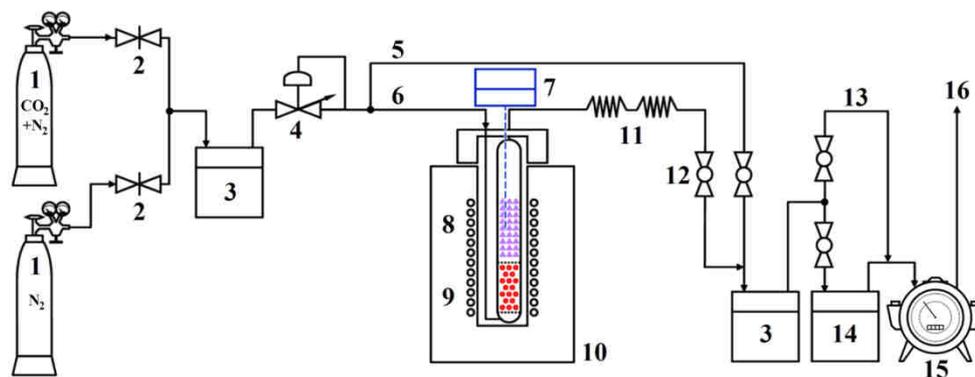


Fig. 2. Scheme of the experimental apparatus: 1 - pressure cylinder with working gas, 2 - needle valve, 3 - mass flow meter, 4 - flow controller, 5 - reactor bypass, 6 - gas inlet, 7 - thermometer, 8 - sorption zone, 9 - preheating zone, 10 - oven, 11 - spiral cooler, 12 - ball valve, 13 - bypass of IR analyser, 14 - IR analyser, 15 - gas meter, 16 - gas outlet (Staf, 2015)

The laboratory apparatus described above enabled, unlike TGA, working with greater amounts of samples and also the conditions of sample exposition to simulated flue gas were much closer to those expected in real operation. The apparatus was designed for operation in atmospheric pressure with loose fill samples of a total volume of 70 ml. The condition for maintaining minimal pressure drop in the reactor was to use such granulometry that would ensure sufficient porosity of the layer. It was empirically determined that operation of the apparatus is best suited by crushed samples sieved to the fraction of 1-2 mm. Given that the bulk density of the samples of this granulometry ranged from 1.29 to $1.42 \text{ g}\cdot\text{cm}^{-3}$, the weight of samples from the individual quarrying localities was 90-100 g.

The calcination phase was carried out in an atmosphere of pure nitrogen, while a mixture of 14 % mol. CO_2 in nitrogen was chosen for carbonation. This atmosphere was to simulate oxygen free flue gases with CO_2 content corresponding with ordinary flue gases in energy production. Different methods for calcination and

carbonation were also selected in the case of heating, with regard to the chemistry of the process and the suggested evaluation method.

For the future application of Ca-looping in industrial practice a stream of CO₂, generated by oxyfuel combustion of suitable sulphur free fuel, is estimated as the calcination atmosphere. However, within this study N₂ flow was chosen for all calcinations due to technical reasons. Pure CO₂ could not be used for calcinations. Otherwise, it would not be possible to quantify the percentage of released CO₂ by means of IR analyser. Testing of various compositions of calcination atmosphere is a subject of the follow-up research.

During calcination, heating was carried out using programmed increase of temperature, with a 10 K.min⁻¹ ramp. Carbonation, on the other hand, was carried out in isothermic conditions. On the basis of TG analysis (Fig. 4), the target temperature necessary for a complete decomposition of all samples was determined as 1273 K. The temperature of isothermic calcination was determined on the basis of study of Berstad et al. (2014) and then experimentally confirmed as 923 K. Volume flow rate of both of the used gases was kept at 2 dm³.min⁻¹. This optimum value was also determined empirically. The flow rate of gas needed to ensure correct measurement by IR analyser ASEKO is approximately 0.8-1.0 dm³.min⁻¹. Too high volume flow rate decreases measurement sensitivity, which can lead to an incorrect assessment of the end of carbonation when the limestone is already almost fully saturated, and the carbonation reaction proceeds very slowly (Fig. 4).



Fig. 3. Photo of the apparatus in operation (Staf, 2016)

One complete cycle of measurements was therefore carried out in the following way. After placing a sample in the apparatus and testing its gas tightness, the nitrogen inlet was connected. The inert gas flowed through the reactor without the furnace heating turned on until the zero signal on the IR analyser stabilised. Furnace heating was then initiated at speed mentioned above and at the same time, data recording began on the IR analyser, thermometer and flowmeter. After the target calcination temperature was reached, the measurement continued until the IR analyser showed again a zero value of CO₂ content in the gas, which indicated the completion of the process of thermic decomposition of the sample. Data collection and furnace heating were then terminated. Nitrogen flowed through the reactor the whole time the reactor was cooling to the preset temperature of carbonation. Before the carbonation phase of the experiment commenced, a control measurement was carried out, which checked the IR analyser response to the flow of gas with the initial CO₂ concentration. During this control measurement, the CO₂ mixture was fed from a pressure bottle through a bypass directly to the analyser. When carbonation temperature was reached, the gas supply valve was switched from N₂ to a CO₂ mixture, and at the same time, the recording of IR analyser, flowmeter and thermometer data was initiated. The carbonation phase continued at a constant temperature until the CO₂ content detected in the gas exiting the reactor was the same as at the inlet from the pressure bottle. This indicated that the sorbent reached a state of

equilibrium saturation and the given experimental cycle could thus be terminated. Furnace heating was then switched off; the reactor was removed from the heated area and left to cool down to laboratory temperature, at which it became ready for the initiation of another experimental cycle. The flow of the CO₂ gas mixture was maintained for the duration of the cooling of the reactor.

For each sample, the blank (dead volume of the apparatus) was measured. The dead volume curve made it possible to determine for each experiment the amount of CO₂ that is apparently sorbed as a result of transport delay which occurs between the moment when the inlet valve with CO₂ mixture is opened, and the moment when the IR analyser detects CO₂ concentration corresponding with the initial composition of the mixture. The measurement of the dead volume of the apparatus was carried out in the reactor in which the sample fully saturated with carbon dioxide was placed. The measurement proceeded as follows. After the first carbonation of a sample, the reactor was left to cool down completely to laboratory temperature. Nitrogen supply was then attached, and its flow was maintained until the value of CO₂ content on the IR analyser reached zero. The gas was then switched to a CO₂ mixture and, at the same time, the recording of gas flow and IR analyser data collection were initiated. The result was a breakthrough curve corresponding to the respective zero sorption capacity of the sample. In the evaluation of each carbonation cycle, the value of apparently sorbed CO₂ was subtracted from the value of sorption capacity of the sample (see below).

A total of six calcination – carbonation cycles was carried out for all samples. Published studies suggest that the greatest decrease in sorption capacity occurs in the first two to three and, apart from some exceptions, no significant decrease is detected after ten and more cycles as pointed by Angeli et al. (2014).

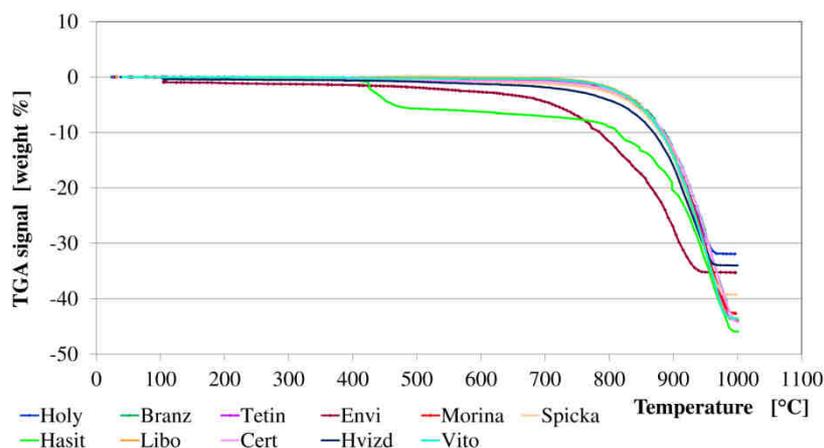


Fig. 4. Comparison of TGA curves measured under N₂ atmosphere.

Mathematical processing of measured data

The output of the measurement was continuously recorded - data about CO₂ content in the gas emerging from the reactor, temperature in a layer of the sample, and volume flow rate of gas through the reactor. The interval of automated data collection was 5s in all three cases. Quantities necessary for the mathematical evaluation of the experiment (i.e. the temperature of the medium in the gasometer, and the pressure of the gas in the apparatus) were discontinuously recorded before each measurement.

The volume of CO₂ sorbed on the known sample weight during the whole time of carbonation was calculated as a sum of partial volumes that were sorbed in individual sampling intervals (5s). The sorbed volume in a sampling interval was calculated using the arithmetic mean of CO₂ content in the exiting gas measured in two subsequent readings. The CO₂ volume corresponding to the measured dead volume of the apparatus was then subtracted from the value of total sorbed CO₂. For a mutual comparison of the samples, the value of sorbed volume was converted, at the given temperature and pressure conditions, to weight relative to 100g of the initial dry sample. Given the fact that the apparatus was working under atmospheric pressure, the equation of state of an ideal gas was used for this conversion with sufficient precision. The calculation method is demonstrated using the following four formulas (Eq. 1 - Eq. 4):

$$\varphi_{CO_2} = Sig_{CO_2} - \varphi_z, \quad (1)$$

$$V_{CO_2,i} = \varphi_b \cdot \frac{V \cdot \tau_s}{60 \cdot 100} - \frac{(\varphi_{CO_2})_{n-1} + (\varphi_{CO_2})_n}{2} \cdot \frac{V \cdot \tau_s}{60 \cdot 100}, \quad (2)$$

$$V_{CO_2} = \left(\sum_i V_{CO_2,i} \right) - V_{CO_2,d}, \quad (3)$$

$$\bar{m}_{CO_2} = \frac{p_r \cdot V_{CO_2} \cdot M_{r,CO_2}}{R \cdot (t + 273,15) \cdot m_s} \cdot 100 \quad (4)$$

where φ_2 is the value of the zero line of IR analyser signal [% CO₂ vol.], φ_b is the value of the base line of IR analyser signal [% CO₂ vol.], Sig_{CO_2} is the value of the 'raw' IR analyser signal [% CO₂ vol.], V is the volume flow rate of gas through reactor [dm³.min⁻¹], τ_s is the sampling interval of analyser (interval of data recording) [s], φ_{CO_2} is CO₂ volume fraction at the outlet of the apparatus [% vol.], $V_{CO_2, i}$ is the volume of CO₂ sorbed in partial interval of data recording [dm³], V_{CO_2} is the total sorbed CO₂ volume [dm³], p_r is the absolute pressure of gas in gasometer [kPa], M_{r,CO_2} is the relative molecular mass of CO₂ [-], t is the temperature of gas in the gasometer [°C], m_s is the sample weight [g], R is the molar gas constant [J.K⁻¹.mol⁻¹], \bar{m}_{CO_2} is the total sorbed weight of CO₂ related to 100g of sample [100g].

For the purposes of mutual comparison of basic characteristics of the samples, Table 1 was created, which summarises data concerning the origin of a sample, its elemental composition, weight change as measured by the TGA method, apparent density, and its theoretical capacity for CO₂ sorption. The apparent density was determined pycnometrically, using heptane as the pycnometric liquid. Taken as the theoretical sorption capacity of each sample was the quantity (i.e. weight) of carbon dioxide that can be released by thermal decomposition of calcium carbonate and magnesium carbonate contained in the original limestone. Contents of these carbonates were calculated on the basis of the Mg and Ca content determined by XRF analysis. This theoretical capacity of the carbonates did not include any other possibilities of chemisorption or physical adsorption.

Tab. 1. Identification and basic properties of the samples.

Sample name	Quarry (locality)	XRF analysis		Theor. capacity for CO ₂ [g.100 g ⁻¹]	Dm TGA [g.100 g ⁻¹]	Apparent density [g.cm ⁻³]
		CaCO ₃ [wt %]	MgCO ₃ [wt %]			
HVIZD	Hvízd'alka	69.32	3.58	32.35	34.02	2.77
SPICKA	Na špičce	78.28	3.31	36.15	39.27	2.74
BRANZ	Branžovy	98.22	0.93	43.67	43.92	2.72
ENVI	Úpohlavy	74.43	1.71	33.62	35.28	2.51
TETIN	Tetín	96.58	1.59	43.29	43.76	2.85
HOLY	Holý vrch	84.24	3.64	38.94	31.93	2.79
MORINA	Mořina	91.47	4.39	42.51	42.64	2.73
CERT	Velkolom Čertovy schody	98.86	0.75	43.86	44.30	2.80
LIBO	Kamenolom Štramberk -Libotín	96.47	1.19	43.04	43.66	2.64
VITO	Vitošov	98.02	0.64	43.44	43.51	2.82
HASIT	Hejtná	82.64	12.49	42.86	45.92	2.77

The evaluation of the measured and mathematically processed values was concluded by the construction of several comparative graphs. Specifically, graphs of breakthrough curves during carbonation, curves of CO₂ release from carbonates during high-temperature calcination of samples, bar graphs comparing sorption capacities determined in the course of cyclic repetition of calcination and carbonation, and line graphs comparing, in the same way, the behaviour of several samples at the same time.

Results and discussion

The shape of breakthrough curves is demonstrated in Fig. 5 by a sample from the Vitošov locality. To demonstrate the shape of CO₂ release curves depending on the instantaneous temperature of calcination, shown in Fig. 6, the selected sample was from the Libotín locality. The sample from quarry Hvízd'alka was used in Fig. 7 as an example of a comparative bar graph of changes of sorption capacities during six cycles of calcination – carbonation. Similarly, the changes of sorption capacities of individual samples during cyclic tests were not only verbally summarised, but also – for the sake of clarity – shown graphically, as evidenced by the example in Fig. 8.

Each limestone from the sample base was subjected to four independent series of sorption properties measurements, including six calcination/carbonation cycles. The below-discussed capacities are represented by the arithmetic mean of the corresponding values, obtained within these four repetitions. Repeatability of the experiments was verified using standard statistical tools, namely calculations of standard deviation and coefficient of variation (CV). In all measured cycles, the percentage values of CV, calculated for sorption capacities as well as for amounts of desorbed CO₂, were in the range from 1.8 % to 7.8 %.

The highest value of sorption capacity for CO₂, in the first as well as in the last of the measured cycles, was determined in the limestone from the quarry Čertovy schody, in which the highest sorption capacity was anticipated on the basis of XRF analysis. The readings for this sample were 37.1 and 15.6 g.100 g⁻¹ of the sample

in the first and the last measured cycle, respectively. The situation was different in the case of the lowest determined sorption capacity. According to the XRF analysis, the lowest value should have been shown by the sample from the Hvíždalka locality; in reality, however, the lowest value was determined in the sample Envicalc from the Úpohlavý locality. Consequently, in the last cycle, this material showed the highest value of CV (7.8 %) within four repetitions of tests.

In the first cycle, this sample allowed the sorption of $6.1 \text{ g} \cdot 100 \text{ g}^{-1}$ of the sample and in the last cycle only $1.2 \text{ g} \cdot 100 \text{ g}^{-1}$.

If the sorption capacities that were actually measured were to be related to the theoretical values, they would – within the entire sample base – range from 18.0 % to 84.6 % of the theoretical values in the first cycle, and from 3.5 % to 35.6 % in the last one.

The average actual sorption capacity in the first cycle was $24.8 \text{ g} \cdot 100 \text{ g}^{-1}$ of the sample and $9.1 \text{ g} \cdot 100 \text{ g}^{-1}$ of the sample in the last cycle.

As it was mentioned above, the stability of the achieved sorption capacity is a key parameter in terms of a practical application of limestones in carbonate looping. If the decrease of this capacity is expressed relatively to the first measured cycle, then the smallest decrease – 57.9 % – was shown by the limestone from the quarry Čertovy schody. Whereas the greatest relative decrease – 66.3 % – was determined in the sample from the Libotín locality. The average relative decrease was 66.9 % of the initially determined capacity.

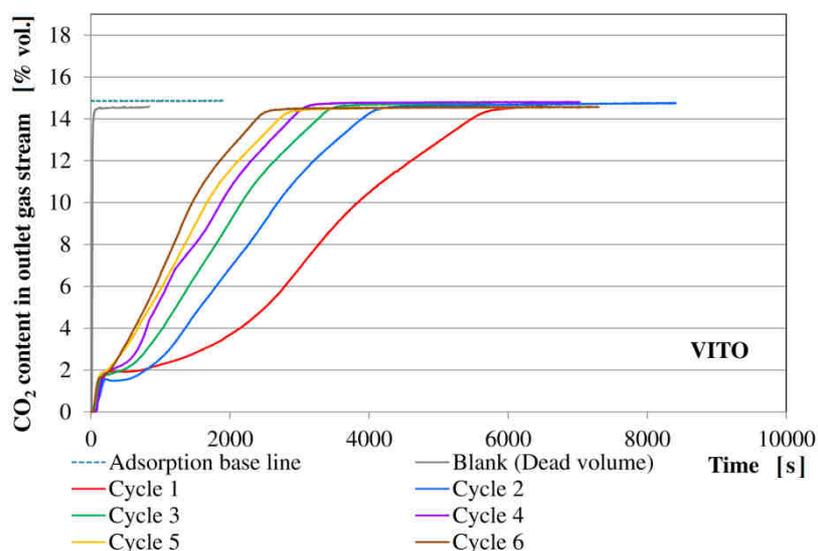


Fig. 5. Shape of breakthrough curves of the sample from the quarry Vitošov.

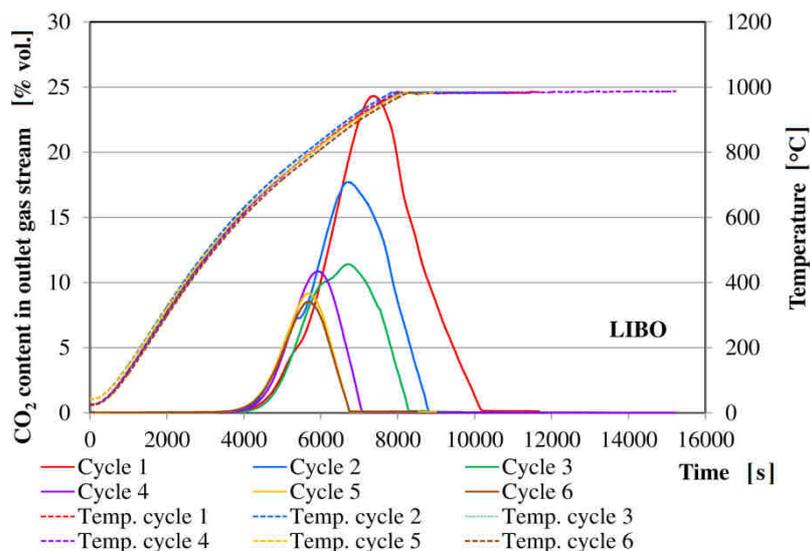


Fig. 6. Course of CO_2 release during calcinations of the sample from the quarry Libotín.

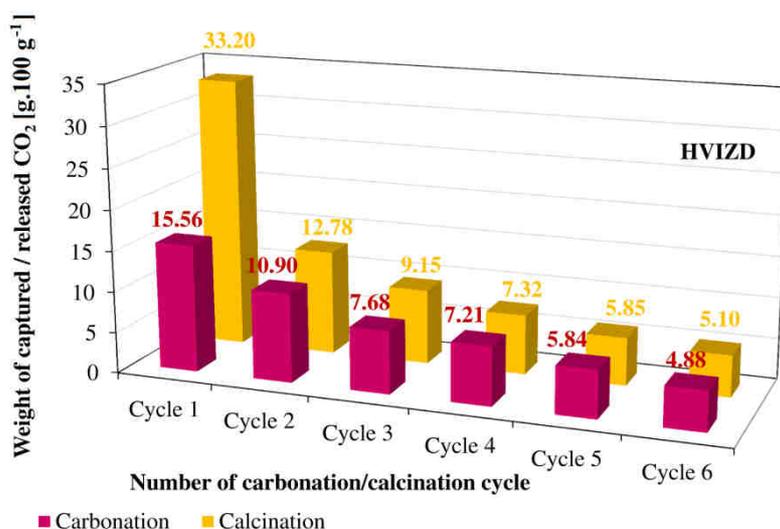


Fig. 7. Comparison of adsorbed and desorbed amounts of CO₂ during tests of the sample from the quarry Hvíždalka.

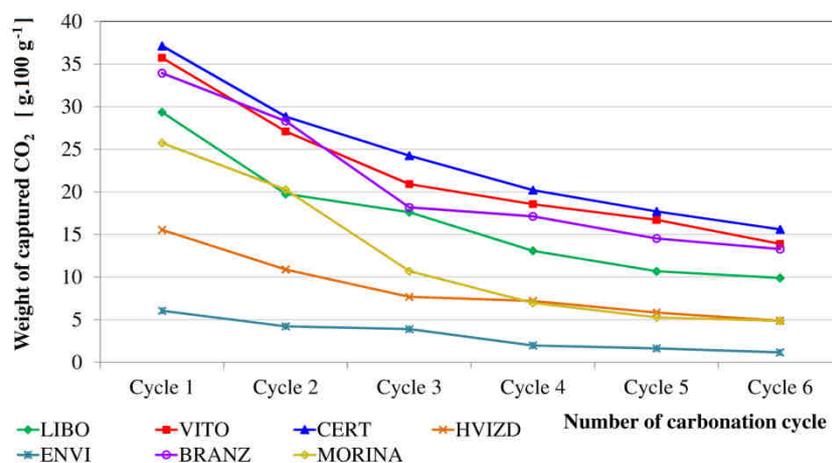


Fig. 8. Comparison of changes in sorption capacities.

Conclusion

The conducted experiments proved that limestones from quarries in the Czech Republic offer a good resource platform for a potential application of carbonate looping technology in post combustion capture of carbon dioxide. On the other hand, it is necessary to pay attention to the selection of a suitable limestone when applied in practice, because the sample base shows great differences not only in sorption capacities but mainly in their subsequent changes during cyclic strain. It is evident that the content of CaCO₃ or MgCO₃ in a limestone is an important – but not the only – parameter which determines sorption capacity and in particular its stability in a regenerative application of limestone. This fact is clearly visible, for example, from the graph in Fig. 7.

Samples from the quarry Čertovy schody and the Libotín locality have very similar CaCO₃ and MgCO₃ contents and corresponding theoretical capacities. Yet the sample from the quarry Čertovy schody showed a capacity that was higher by 7.8 g.100 g⁻¹ of the sample in the first cycle, and by 5.7 g.100 g⁻¹ of the sample in the last cycle.

The results of this study were in agreement with the findings in available literary resources, namely in studies written by Manovic et al. (2008), Lu et al. (2006), Berstad et al. (2014), but their evaluation generated further questions, which are to be the subject of subsequent research. Thanks to a broad sample base and detailed data concerning the origin and composition of the tested samples, the conducted tests provided a good platform for designing a carbonate looping semi-industrial unit which uses limestones from local sources in the Czech Republic. From the follow-up research activities intended for the near future, the following should be mentioned.

First of the follow-up activities will be calcination experiments conducted in order to determine the exact causes of deactivation. The reason for that are the not quite consistent results of already published studies of Feng et al. (2006), Angeli et al. (2014) or Berstad et al. (2014), which mention as the causes of the reduction of

sorption capacity during cyclic strain, apart from sintering, also structural causes leading to a mechanical blockage of some pores.

To assess the influence of sintering and pore blockage, the experiments will measure the changes of specific surface, distribution and size of pores and crystallinity (according to XRD) depending on the changing maximum calcination temperatures. If a favourable effect is proved of the reduction of calcination temperature on limiting the loss of sorption capacity, multi cyclic tests will follow, examining the extension of the lifespan of a limestone batch.

Also, the possibility of inexpensive reactivation of partially debased limestone will be tested by means of hydration at low temperatures by liquid water and increased temperatures by water steam fed into a layer of sorbent. Part of this phase of research will be the assessment of the influence of unwanted contamination of calcined material by residual concentrations of products of fossil-fuel combustion, such as dust particles and low concentrations of unseparated SO₂.

One of the partial tasks will also be the determination, whether the presence of minor elements and their inorganic compounds influences changes in sorption capacity and the process kinetics.

An important point which needs to be examined is also the testing of the course of calcination and carbonation in the same atmosphere, simulating flue gas containing CO₂. A positive test result would bring a financial saving in a subsequent application of the technology into practice.

In a medium term horizon, a conversion is planned of the above described experimental apparatus for operation under an increased pressure of gaseous media.

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