

## REMOVING CARBON DIOXIDE FROM FLUE GAS USING HIGH TEMPERATURE CARBONATE LOOPING

Karel Ciahotný<sup>a</sup>, Marek Staf<sup>a</sup>, Tomáš Hlinčík<sup>a</sup>, Veronika Vrbová<sup>a</sup>, Lenka Jílková<sup>a</sup>, Simona Randáková<sup>b</sup>

<sup>a</sup>Department of Gas, Coke and Air Protection,

University of Chemistry and Technology Prague, Technická 5, 166 28 Praha 6

<sup>b</sup>Central laboratories, University of Chemistry and Technology Prague, Technická 5, 166 28 Praha 6

e-mail: Karel.Ciahotny@vscht.cz

The article describes the basics of the process of high temperature carbonate looping, which is being developed as one of the methods of CO<sub>2</sub> capture from flue gas produced during fossil fuel combustion. Used as adsorbents in this process are mainly alkaline-earth metal oxides, most frequently CaO. A reaction of the sorbent with carbon dioxide occurs under suitable reaction conditions, producing the respective carbonate. As this involves chemical bonding of CO<sub>2</sub>, the adsorption capacity of the sorbent for CO<sub>2</sub> is high. The sorbent is regenerated by increasing the temperature above the temperature of stability of the given carbonate, which causes the carbonate to decompose into an oxide, and CO<sub>2</sub> is released in a concentrated form. Because the system operates at high temperatures above 600 °C, it is possible to use the residual heat from the process of carbonate looping for the production of electrical energy in a steam cycle. The article describes the results of laboratory tests of limestone samples from various localities in the Czech Republic, which were tested for CO<sub>2</sub> capture in the process of high temperature carbonate looping. The limestone samples were also analysed by the method of elemental analysis, and the CO<sub>2</sub> content was determined which is released when heated above the stability limit of the carbonates present in the limestone sample. The results were then compared with the theoretical sorption capacities of the individual samples for CO<sub>2</sub>, and all cases showed a good correspondence between the measured and the calculated values. Also measured were the adsorption capacities of the individual limestone samples after their previous activation (conversion into oxides) and the acquired results were again compared with the theoretical sorption capacities for CO<sub>2</sub> calculated from the composition of individual samples. The selected adsorbent samples were further tested by measuring breakthrough curves for CO<sub>2</sub> from a model gas mixture containing ca 14% vol. CO<sub>2</sub>, and sorption capacities of samples for CO<sub>2</sub> for the given experimental conditions were then calculated from the measured breakthrough curves.

Keywords: carbonate looping, carbon dioxide, CO<sub>2</sub> capture

Received 10. 10. 2015, accepted 14. 11. 2015

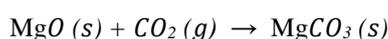
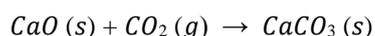
### 1. Introduction

In recent years, first power plants have started to operate that include flue gas cleaning as well as technologies for capturing carbon dioxide. One of the technologies being developed for this purpose is the technology of high temperature carbonate looping. This technology is based on capturing CO<sub>2</sub> from flue gas, using its chemisorption on suitable materials at high temperatures.

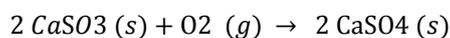
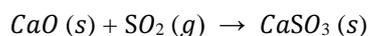
The article describes the fundamentals of the process of high temperature carbonate looping and the results of laboratory tests of limestones from various localities in the Czech Republic which were tested for that purpose in laboratory conditions.

### 2. The principle of high temperature carbonate looping

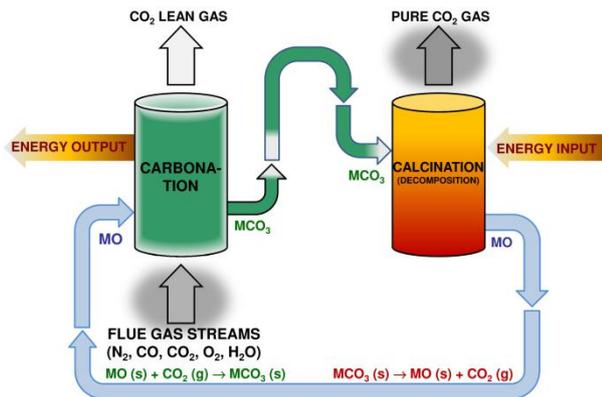
High temperature carbonate looping is one of the ways of removing CO<sub>2</sub> from gases using its chemisorption on metal oxides [1]. The substances which are used most frequently as sorbents are those based on CaO (MgO). Their reactions with CO<sub>2</sub> occur at high temperatures (450 – 750 °C) and are called carbonation; these are exothermic reactions.



Similar to CO<sub>2</sub>, the SO<sub>2</sub> present in flue gas also reacts with metal oxides.



The sorbent is regenerated by heating it to temperatures above the limit of thermal stability of the carbonate (800 – 900 °C), which causes thermal decomposition of the carbonates; the reaction is called calcination and it is endothermic. Sulphates do not decompose at these temperatures; it is therefore necessary to separate them and replace them with new adsorbent. The process of high temperature carbonate looping is schematically depicted in Fig. 1 [2]. An advantage of this process is the high sorption capacity of the adsorbent for CO<sub>2</sub>, which follows from the chemical bond of CO<sub>2</sub> (stable products are formed at a given temperature during a chemical reaction of metal oxides with CO<sub>2</sub>).



**Fig. 1** Outline of the high temperature carbonate looping process

This process usually occurs in a fluidized bed, which is characterized by intensive exchange of mass and heat; it is therefore possible to achieve a high degree of CO<sub>2</sub> removal from flue gas in an apparatus of an acceptable size, even for large quantities of flue gas produced by a large power plant block [3, 4]. Another advantage is the process of flue gas desulphurization that takes place simultaneously because, as mentioned before, sulphur dioxide reacts with alkali metal oxides and alkaline earth metals in a way similar to carbon dioxide.

### 3. Experimental part

This work tested limestone samples from various Czech suppliers for the purposes of their use in the process of high temperature carbonate looping. The aim of the tests was to find limestones with the highest possible adsorption capacity for CO<sub>2</sub>.

#### 3.1. Selecting samples for testing

During the selection of limestone samples suitable for high temperature carbonate looping such materials were chosen that are available at the Czech market in large quantities. A list of the largest companies in the Czech Republic that quarry materials based on limestone is given in Tab. 1 [5].

A total of 11 limestone samples from various suppliers suitable for high temperature carbonate looping was selected for testing. The necessary information about all samples is summarized in Tab. 2.

#### 3.2. Sample modification before testing

Before testing, the limestone samples were crushed in a jaw mill and then sieved to grain size fractions optimal for the individual tests and analyses. The fractions were: under 0.2 mm; 0.2 – 0.5 mm; 0.5 – 1 mm a 1 – 2 mm.

#### 3.3. Methods of analysis and testing

The purpose of the laboratory tests was to evaluate the usability of the individual limestone samples in the process of high temperature carbonate looping.

**Tab. 1** Overview of limestone suppliers in the Czech Republic [5]

Company	Exploited amount [t/year]	Share in mining [%]
Vápenka Čertovy schody	1 570 000	18
Lafarge Cement	1 189 660	14
Českomoravský cement	1 110 800	13
Holcim	961 000	11
Cement Hranice	841 120	10
Vápenka Vitošov	756 000	9
Lomy Mořina	622 700	7
Kotouč Štramberk	612 500	7
Omya	334 000	4
Hasit	288 000	3

**Tab. 2** Limestones selected for testing in high temperature carbonate looping

Company	Quarry	Sample identification
Českomoravský cement	Hvízdalka	HVIZD
Českomoravský cement	Na Špičce	SPICKA
Českomoravský cement	Branžovy	BRANZ
Lafarge Cement	Úpohlavy	ENVI
Lomy Mořina	Tetín	TETIN
Lomy Mořina	Holý vrch	HOLY
Lomy Mořina	Mořina	MORINA
Vápenka Čertovy schody	Čertovy schody	CERT
Libotín		LIBO
Vitošov	Vitošov	VITO
Hasit	Hejná	HASIT

The following analytical methods were used for the laboratory tests of the selected limestone samples.

#### X-ray fluorescence analysis

This method was used for determining the elemental composition of the limestone samples used for testing. The X-ray fluorescence analysis of limestone samples was performed on the ARL 9400 apparatus. On the basis of CaO and MgO content in the analysed sample it is possible to estimate the carbonate content, providing that the entire quantity of these oxides is transformed into carbonates. The analyser is for these purposes equipped with a special programme that enables a direct calculation of carbonate content in the sample.

#### BET-surface measurement

The characteristics of the porous structure of adsorbent samples were determined by the Coulter SA 3100 (Beckman Coulter) analyser. The analyser operates on the principle of physical adsorption of N<sub>2</sub> from the gas phase at the temperature of 77K. Prior to the testing, the

samples of material were dried at the temperature of 105 °C, and then each sample was precisely weighed into a special container and deaerated at 150 °C in a high vacuum for at least 240 minutes. After the deaeration, the sample in the container was weighed again and the container was placed in the measuring port of the apparatus and immersed in liquid nitrogen. In the apparatus the sample was again evacuated into high vacuum. After the evacuation, precisely measured volumes of gaseous nitrogen from the dosage device were released in stages to the sample. Following each stage, equilibrium pressure in the vicinity of the adsorbent was measured and the adsorbed amount of nitrogen was calculated from it. The measurement was evaluated from the shape of adsorption and desorption isotherms. For the range of relative pressures 0 – 0.3 the quantities of adsorbed nitrogen were evaluated using a BET equation, and the coefficients were used to determine the BET-surface of the material.

#### Determining CO<sub>2</sub> content using elemental analyser

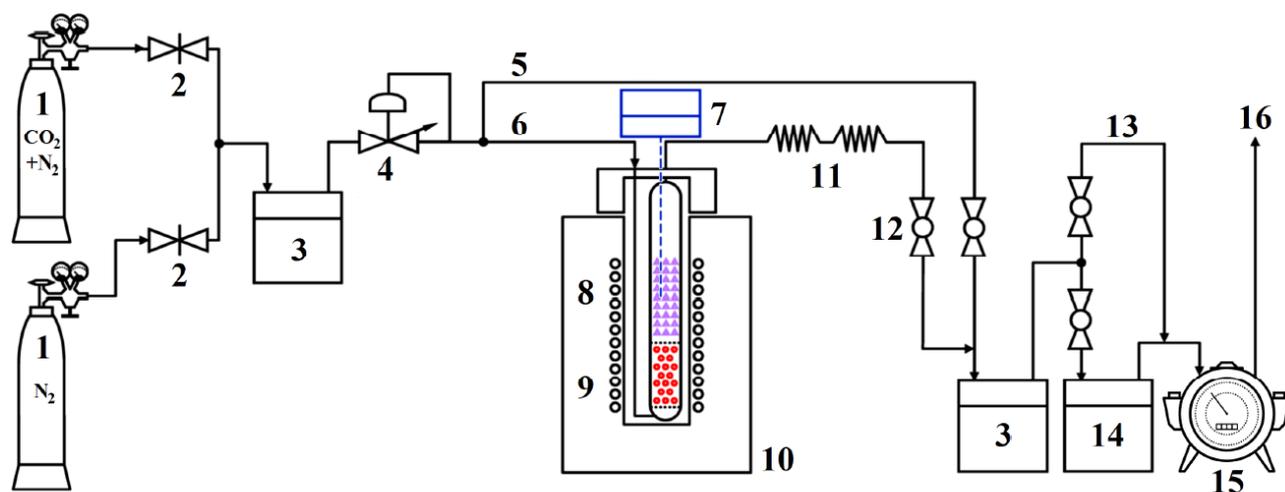
To determine the CO<sub>2</sub> content in limestone samples, the method of elemental organic analysis on a Thermo Scientific Flash 1112 apparatus was used. The principle of this method is burning a sample in a combustor in a stream of oxygen at a high temperature (ca 1600 °C), subsequent catalytic reduction of some of the combustion products, separation of the individual products in short chromatographic column, followed by detection and determining the content on a TCD detector. The working range of the apparatus is 0.01 – 100% for each determined component (C, H, N, S). In the case of limestone samples, these are inorganic materials, but when they are heated, CO<sub>2</sub> is released and subsequently determined by the apparatus, similarly to CO<sub>2</sub> that is produced by carbon combustion.

#### Measuring CO<sub>2</sub> sorption capacity

The carbonation of the samples of CaO prepared from the individual limestone samples by calcination at 1000 °C in a muffle furnace was carried out on the Quantachrome ASiQ sorption system. Before the measurements each sample was first flushed with helium in the sampling cell. This was followed by evacuating the cell and heating the sample to 650 °C. Exactly measured volumes of CO<sub>2</sub> were gradually released into the cell during the testing. After equilibration, the equilibrium pressure of CO<sub>2</sub> in the system was deducted and subsequently next volume of CO<sub>2</sub> was then dosed; the whole sorption isotherm was measured in this way. The apparatus makes it possible with a special programme to determine the share of chemisorption and physical adsorption for individual equilibrium pressures.

#### Determining adsorption capacity for CO<sub>2</sub> on a flow apparatus with a fixed bed of sorbent

To study the sorption of carbon dioxide from a model gas mixture, a flow laboratory apparatus with a fixed layer of adsorbent was designed; it is outlined in Fig. 2. The tested limestone samples were calcined in this apparatus, just as the subsequent sorption of CO<sub>2</sub> from the model gas mixture. A cylindrical electric furnace, placed on a mechanical lever, was used for heating the material to high temperatures. This enabled faster cooling of the apparatus after the calcination phase of the process ended. The samples were calcined in an inert nitrogen atmosphere, while the carbonation phase was carried out in a gas atmosphere, 14% vol. of which was carbon dioxide in a mixture with nitrogen.



**Fig. 2** Outline of the laboratory apparatus used for testing the adsorbents for CO<sub>2</sub> capture

(1 – pressure bottle with gas, 2 – needle valve, 3 – flow meter, 4 – flow regulator, 5 – bypass, 6 – gas inlet into the reactor, 7 – thermometer, 8 – ads. zone with sample, 9 – preheating zone, 10 – electric heating furnace, 11 – air coolers, 12 – ball valve, 13 – gas flow splitting, 14 – CO<sub>2</sub> analyser, 15 – wet gas meter, 16 – gas outlet)

All gas distribution systems in the apparatus were made from stainless steel capillary tubes Swagelok 6mm (interior diameter 4mm). The individual components were arranged in the direction of gas flow as follows. The gases were fed from pressure bottles via flexible tubes through a pair of manual needle valves into a digital flow regulator Bronkhorst EL-FLOW Select, which also functioned as a flowmeter. The flow of the gas was then split into two, with one branch directed to a high temperature reactor and the other branch working as a by-pass for the purposes of measuring CO<sub>2</sub> concentration in the model gas mixture before the adsorber.

The high temperature cylindrical reactor was made of quartz glass and in its axis was installed a NiCr-Ni thermocouple connected to a digital thermometer/data-logger Greisinger GMH 3250, which provided continuous measurement and recording of temperature in the sample layer. This construction solution made it possible to calcine limestone samples to the end temperature of 1000 °C. The gas exiting the spiral coolers was cooled down in air coolers.

The content of carbon dioxide in the gas behind the adsorber was continuously measured by ASEKO AIR-LF infrared analyser. Given the fact that the accuracy of determining sorption capacity depends mainly on a precise measurement of the volume of gas flowed through the apparatus, a wet drum gas meter was connected to the end of the apparatus.

## 4. Results and discussion

### *X-ray fluorescence analysis*

In the whole group of analysed limestone samples only those chemical elements were monitored for which the mass content of at least one sample exceeded the value of 0.1% wt. Values converted to carbonates and normalized for 100% were used as the assessment base. The results of the analyses are given in Tab. 3. The theoretical CO<sub>2</sub> sorption capacities of individual samples calculated from their composition are given in Tab. 4.

**Tab.3** X-ray fluorescence analysis of limestone samples selected for testing

Sample:	Morina	Tetin	Envi	Spicka	Hvizd	Branz	Holy	Cert	Libo	Vito	Hasit
Component	Content in sample [% wt.]										
MgO	2,10	0,76	0,82	1,58	1,71	0,44	1,74	0,36	0,57	0,31	5,97
Al <sub>2</sub> O <sub>3</sub>	1,22	0,44	6,11	4,95	3,94	0,21	1,04		0,43	0,37	0,78
SiO <sub>2</sub>	2,13	0,86	14,88	10,29	20,26	0,32	10,32	0,18	1,07	0,73	3,11
P <sub>2</sub> O <sub>5</sub>	0,16	0,18	0,12				0,11		0,61		
S			0,12		0,29						
K <sub>2</sub> O	0,17		0,94	0,10	0,69		0,22				
CaO	51,25	54,11	41,70	43,86	38,84	55,03	47,20	55,39	54,05	54,92	46,30
TiO <sub>2</sub>			0,24	0,24	0,30						
Fe <sub>2</sub> O <sub>3</sub>	0,35	0,20	1,25	1,79	1,37	0,17	0,29			0,12	0,36

**Tab. 4** Theoretical CO<sub>2</sub> sorption capacities of limestone samples selected for testing

Sample	Determined content [% wt.]			Calculated content [% wt.]			Theor. sorption capacity for CO <sub>2</sub> [% wt.]		
	MgO	CaO	Ca	Mg	CaCO <sub>3</sub>	MgCO <sub>3</sub>	from CaO	from MgO	Total
HVIZD	1,71	38,84	27,76	1,03	69,32	3,58	30,48	1,87	32,35
SPICKA	1,58	43,86	31,35	0,95	78,28	3,31	34,42	1,73	36,15
BRANZ	0,44	55,03	39,33	0,27	98,22	0,93	43,19	0,48	43,67
ENVI	0,82	41,70	29,80	0,49	74,43	1,71	32,73	0,89	33,62
TETIN	0,76	54,11	38,67	0,46	96,58	1,59	42,47	0,83	43,29
HOLY	1,74	47,20	33,73	1,05	84,24	3,64	37,04	1,90	38,94
MORINA	2,10	51,25	36,63	1,27	91,47	4,39	40,22	2,29	42,51
CERT	0,36	55,39	39,59	0,22	98,86	0,75	43,47	0,39	43,86
LIBO	0,57	54,05	38,63	0,34	96,47	1,19	42,42	0,62	43,04
VITO	0,31	54,92	39,25	0,19	98,02	0,64	43,10	0,34	43,44
HASIT	5,97	46,30	33,09	3,60	82,64	12,49	36,34	6,52	42,86

According to the RDX analyses and the CO<sub>2</sub> adsorption capacities calculated from these analyses, the highest CO<sub>2</sub> sorption capacity was shown by the samples labelled as VITO (43.4% wt.), (BRANZ (43.7% wt.), and CERT (43.9% wt.). The lowest CO<sub>2</sub> sorption capacities, on the other hand, were calculated from the RDX analyses for samples labelled as HVIZD, ENVI and SPICKA.

The content of CO<sub>2</sub> in the individual limestone samples determined by the method of elemental organic analysis is given in Tab. 5. The respective values determined on the basis of the results of RDX analyses of individual samples are also included in the table for comparison.

**Tab. 5** CO<sub>2</sub> content in limestone samples estimated by their elementary analysis

Sample	CO <sub>2</sub> content in % wt.		
	Elemental analysis	RDX	Difference in % rel.
HOLY	36,20	38,94	-7,05
SPICKA	37,93	36,15	4,91
TETIN	43,66	43,29	0,86
MORINA	42,78	42,51	0,63
ENVI	33,61	33,62	-0,03
HASIT	43,23	42,86	0,86
BRANZ	43,81	43,67	0,32
LIBO	43,09	43,04	0,12
HVIZD	33,26	32,35	2,80
VITO	43,48	43,44	0,08
CERT	44,03	43,86	0,39

It is evident from Tab. 5 that the CO<sub>2</sub> content in the individual limestone samples determined by elemental analysis show, with one exception (HOLY), a very good correspondence with the results obtained by RDX fluorescence. In a majority of cases, the difference between the values obtained by the two methods is less than 1% rel.

Tab. 6 shows the results of CO<sub>2</sub> adsorption capacities of individual samples measured at 650 °C by the Quantachrome ASiQ apparatus. The measured adsorption capacities for CO<sub>2</sub> were related to CaO and then converted to CaCO<sub>3</sub> to enable a comparison of the measurement results with the results determined by RDX analyses and elemental analyses of limestone samples.

The correspondence of the results of adsorption capacities for CO<sub>2</sub> determined by measurements on the Quantachrome apparatus with the amount of CO<sub>2</sub> bound in the original limestone samples is not so good in this case and the sorbed quantities of CO<sub>2</sub> show lower values compared to the CO<sub>2</sub> that was originally bound in the limestone samples. This is caused by the fact that the chemical bond of CO<sub>2</sub> does not use the entire capacity of the adsorbent, perhaps because a certain part of it is deactivated by the sintering of the surface of the material at high temperatures [6, 7].

**Tab. 6** Adsorption capacities of limestone samples for CO<sub>2</sub> estimated by Quantachrome analyzer

Sample	CO <sub>2</sub> content [% wt.]		Ads. capacity for CO <sub>2</sub> [% wt.] Quantachrome
	Element. analysis	RDX	
HOLY	36,20	38,94	20,29
SPICKA	37,93	36,15	30,3
TETIN	43,66	43,29	36,62
MORINA	42,78	42,51	36,02
ENVI	33,61	33,62	11,94
HASIT	43,23	42,86	28,35
BRANZ	43,81	43,67	34,14
LIBO	43,09	43,04	37,21
HVIZD	33,26	32,35	19,69
VITO	43,48	43,44	33,89
CERT	44,03	43,86	36,40

The results of measurements of BET-surface of the original limestone samples, samples after calcination at 1000 °C and calcined samples after CO<sub>2</sub> exposition on Quantachrome are given in Tab. 7.

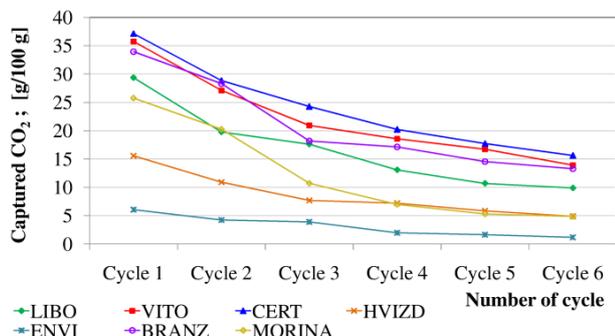
**Tab. 7** BET-surface of limestone samples, samples after calcination and samples after CO<sub>2</sub> saturation

Sample	BET-surface [m <sup>2</sup> ·g <sup>-1</sup> ]		
	Original sample	After calcination at 1000 °C	After CO <sub>2</sub> adsorption
HOLY	1,04	1,40	0,52
SPICKA	3,24	2,43	0,59
TETIN	0,45	3,44	0,14
MORINA	1,39	2,41	0,57
ENVI	14,53	2,63	0,51
HASIT	0,12	4,92	0,25
BRANZ	0,26	3,37	0,40
LIBO	0,39	3,49	0,56
HVIZD	3,27	1,62	0,58
VITO	0,34	5,74	0,44

Tab. 7 shows that the inner surface of most samples is increased during calcination. Exceptions to that are the samples SPICKA, ENVI and HVIZD. The last two samples are characterized by the fact that their sorption capacity for CO<sub>2</sub> determined on Quantachrome is considerably lower than their theoretical sorption capacity. Both the samples show, compared to the other samples, high potassium content, which probably causes partial sintering of the outer surface of the particles of the material during its calcination and thus a decrease of reactivity of the calcined sample of material to CO<sub>2</sub>.

Fig. 3 shows the results of measurements adsorption capacity of the calcined samples prepared from individual limestone samples by calcination at 1000 °C and testing of the calcined materials on a flow apparatus with a

fixed layer of adsorbent. The figure shows very well the decrease in sorption capacity of the samples in repeated cycles of carbonation (CO<sub>2</sub> adsorption) – calcination (CO<sub>2</sub> desorption). The results of all measurements were in this case also converted to carbonates as the basis, in order to make them comparable with the results obtained by the methods mentioned earlier.



**Fig. 3** Adsorptions capacities for calcinated limestone samples for CO<sub>2</sub> in repeated adsorption – desorption cycles

The adsorption capacities for CO<sub>2</sub> determined for the first adsorption cycle on a flow laboratory apparatus correspond relatively well with the results of measurements on Quantachrome ASiQ. But it must be borne in mind that this apparatus uses pure CO<sub>2</sub> for the measurements.

With an increasing number of adsorption – desorption cycles all of the tested samples show a decrease in their adsorption capacity for CO<sub>2</sub>, which is probably caused by the sintering of the surface of the particles of material, which thus becomes non-reactive. This is consistent with the information published about this topic in the scientific literature.

From the tested samples, the highest sorption capacities for CO<sub>2</sub> and the lowest decrease of sorption efficiency in repeated cycles was shown by the limestones from quarries Čertovy schody, Vitošov and Branžovy. Samples from quarries Libotín, Mořina and Tetín also show high sorption capacities for CO<sub>2</sub>. Samples labelled as ENVI (Lafage Cement), HVIZD (Českomoravský cement) and HOLY (Holý vrch, Lomy Mořina), on the other hand, proved unsuitable for use in the process of high temperature carbonate looping.

## 5. Conclusion

A total of 11 limestone samples from various localities in the Czech Republic were tested in laboratory conditions for the purposes of use in the process of high temperature carbonate looping. The tests focused on determining the composition of the samples and the content of bound CO<sub>2</sub> (RDX fluorescence and elemental analysis), the porous structure (N<sub>2</sub> adsorption at 77 K) and the adsorption capacity for CO<sub>2</sub> at 650 °C (measuring CO<sub>2</sub>

chemisorption on Quantachrome apparatus and measuring CO<sub>2</sub> breakthrough curves on a flow apparatus with a fixed layer of adsorbent).

It was found that both RDX analysis and elemental analysis are suitable methods for determining the content of CO<sub>2</sub> bound in the samples of adsorbent. The results of measurements obtained by these methods show in a majority of samples a deviation lower than 1% rel.

The highest sorption capacities for CO<sub>2</sub> were shown by limestone samples from the localities Čertovy schody, Vitošov and Branžovy. These samples are capable of sorbing ca 34 to 37g of CO<sub>2</sub> for 100g of limestone. This sorption capacity corresponds to about 80% of theoretical CO<sub>2</sub> content in the individual limestone samples used for testing. The chemisorption capacity of the adsorbent samples for CO<sub>2</sub> decreases in repeated cycles of chemisorption – calcination. The results of measurements obtained on a flow apparatus are similar to the results that were obtained using the Quantachrome ASiQ apparatus, although the correspondence is not nearly as good as in the case of testing using the methods of RDX analysis and elemental analysis. This is probably caused by the fact that each of the methods used for measuring CO<sub>2</sub> chemisorption operates under different conditions (at a different part. pressure of CO<sub>2</sub>). Most limestone samples show an increase of inner BET-surface during calcination, with the exception of samples SPICKA, ENVI and HVIZD. The last two samples are characterized by a high potassium content, which is probably the cause of the sintering of outer surface of the samples during calcination at 1000 °C. This leads to a decrease in the reactivity of calcined samples with CO<sub>2</sub>. Samples after a reaction with CO<sub>2</sub> show a lower inner surface than the calcined samples and the original limestone samples. The adsorption capacity of all samples of material decreases with the repetition of the samples of calcination – CO<sub>2</sub> adsorption, which is attributed to the sintering of their outer surface.

## Acknowledgements

The results presented in this article were obtained as parts of the projects ‘Researching high temperature sorption of CO<sub>2</sub> from flue gas using carbonate looping’ and ‘The low emission power plant system including pre combustion CO<sub>2</sub> capture’. The research was partially funded using a Norwegian grant (project no.: NF-CZ08-OV-1-005-2015) and the grant TAČR (project No TA04021005).

## Literature

- Choi, S.; Drese, J. H.; Jones, Ch. W. Adsorbent Materials for Carbon Dioxide Capture from Large Anthropogenic Point Sources. *Chem. Sus. Chem* 2009, 2 (9), 796–854.
- Gomes, J. F. P. Carbon Dioxide Capture and Sequestration: An Intergrated Overview of Available Technologies; Nova Science Publishers, 2013.

3. Ströhle, J.; Lasheras, A.; Galloy, A.; Epple, B. Simulation of the carbonate looping process for post-combustion CO<sub>2</sub> capture from a coal-fired power plant. *Chemical Engineering and Technology* 2009, 32 (3), 435–442.
4. Ströhle, J.; Galloy, A.; Epple, B. Feasibility study on the carbonate looping process for postcombustion CO<sub>2</sub> capture from coal-fired power plants. *Energy Procedia* 2009, 1 (1), 1313–1320.
5. Štramberská, K. Těžba vápenců v České republice, diplomová práce. Diplomová práce, Universita Palackého v Olomouci, 2008.
6. Feng, B.; Liu, W.; Li, X.; An, H. Overcoming the Problem of Loss-in-Capacity of Calcium Oxide in CO<sub>2</sub> Capture. *Energy Fuels* 2006, 20 (6), 2417–2420.
7. Grasa, G. S.; Abanades, C. CO<sub>2</sub> Capture Capacity of CaO in Long Series of Carbonation/Calcination Cycles. *Ind. Eng. Chem. Res.* 2006, 45 (26), 8846–8851.

### Summary

*Karel Cíahotný, Marek Staf, Tomáš Hlinčík, Veronika Vrbová, Lenka Jílková, Simona Randáková*  
*University of Chemistry and Technology Prague, Technická 5, 166 28 Prague 6, ciahotnk@vscht.cz*

#### ***Carbon dioxide removal from flue gas using high temperature carbonate looping***

In the article the basic principles of the high-temperature carbonate looping process are described. This process is being developed as one of the methods of CO<sub>2</sub> capture from flue gases resulting from the combustion of fossil fuels. This process uses mainly the oxides of alkaline earth metals as the adsorbent, most often CaO. Under suitable reaction conditions the sorbent reacts with carbon dioxide leading to the formation of carbonate. Because it is a chemical binding of CO<sub>2</sub>, the adsorption capacity of sorbent for CO<sub>2</sub> is rather high. Sorbent regeneration is done by raising the temperature above the temperature stability of the carbonate, to cause the degradation (calcination) of carbonate to the metal oxide and release of CO<sub>2</sub> in concentrated form. Because the system operates at high temperatures above 600 °C, it is possible to use residual heat from the carbonate looping process for the production of electric energy in the steam cycle. The article describes the results of laboratory tests of limestone samples from different sites in the Czech Republic for the usage in the process of high-temperature carbonate looping. The theoretical sorption capacities for CO<sub>2</sub> of individual samples were estimated from their chemical composition. The samples were analyzed simultaneously by the method of elemental analysis and detected for each sample was the content of CO<sub>2</sub> that is re-

leased when the sample is heated above the limit of stability of carbonates contained in the limestone sample. The estimated results were compared with the theoretical sorption capacity for CO<sub>2</sub> of the samples; in all cases very good correspondence between the measured and calculated values was found. The adsorption capacities of tested samples for CO<sub>2</sub> were measured after their previous calcination and the results were compared again with theoretical adsorptive capacity for CO<sub>2</sub>, calculated from the composition of individual samples. Selected samples of the adsorbents were further tested by the measurement of breakdown curves for CO<sub>2</sub> using the model gas mixture containing CO<sub>2</sub>.