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## APPLICATION OF MODIFIED CALCIUM SORBENTS IN CARBONATE LOOPING

**Michalina KOTYCZKA-MORANSKA, Grzegorz TOMASZEWICZ**

Institute for Chemical Processing of Coal, Zamkowa 1, 41-801 Zabrze, Poland, mmoranska@ichpw.zabrze.pl

**Abstract:** Reduction of CO<sub>2</sub> emission is essential. In this paper, a study of the behaviour of modified Polish CaO-based sorbents during calcium looping cycles has been discussed. All the related tests were conducted using the Netzsch STA 409PG Luxx thermogravimetric analyser. Samples with a weight of  $m_s=10.0\pm 0.1$  mg were placed in an Al<sub>2</sub>O<sub>3</sub> crucible. The calcium looping processes were performed at the carbonation temperature of 650°C and the calcination temperature of 900°C. Additionally, calcination-carbonation cycles with different gas flows were examined. The authors investigated the influence of CO<sub>2</sub> concentration and total gas flow on the carbonation conversion. Sorbents were studied by TG and porosimetry analysis.

**Keywords:** *calcium looping, CO<sub>2</sub> capture, CaO-based sorbents*

### Introduction

It is commonly known that the rising emission of greenhouse gases causes deterioration of the global environment. In order to maintain a balanced living surrounding, mankind must control the emission of CO<sub>2</sub>, being the main component of greenhouse gases, into the atmosphere (Wang and Lee, 2009). Using chemically and physically modified CaO samples in the Calcium Looping Process can be a good opportunity to enhance the CO<sub>2</sub> capture. Intensive research has been carried out to improve the performance of CaO-based sorbents by enhancing the CaO conversion and reducing the performance decay. It is expected that the use of modified sorbents will facilitate increasing the effectiveness of the CO<sub>2</sub> capture and improve sorbents parameters. Application of different methods aimed at increasing porosity and surface area of sorbents to enhance the conversion is a very interesting option. A carbonation process takes place in micropores, on mesopores and on grain boundaries (Bouquet et al., 2009; Manovic and Anthony, 2008). Carbonation in micropores proceeds up to pore filling. The CO<sub>2</sub> capture efficiency depends on many parameters, e.g. diffusion resistance, which depends on the size of the sorbent particles, volume and the pore

structure as well as the surface size and reaction kinetics (Hughes et al., 2004). Under numerous studies, the  $\text{CaCO}_3$  layer diffusion rates as a function of  $\text{CO}_2$  pressure, temperature and  $\text{CaCO}_3$  porosity were examined (Mess et al., 1999). Also Oakeson and Culter (1979) studied nonporous sorbents, and their results confirmed a parabolic particle size. They formulated a law independent of the reaction rate. The particle size of pore and surface area changed in every run of the process. They also found that the  $\text{CO}_2$  pressure has a major effect on the process rate (Oakeson et al., 1979). Bhatia and Perlmutter (1983) modelled limestone using a random pore model and found that the diffusion controlled stage was independent of the  $\text{CO}_2$  pressure. They assumed that the carbonate product layer formed concentric shells parallel to the initial gas.

Sun et al. (2007) describe a mechanism of the limestone reactivity loss during consecutive cycles related to the changes in its porosity. They distinguish between two types of pores: the smaller ones (<200 nm) as type 1 and the larger ones (> 200 nm) as type 2. The authors claim that some of pores of the second type have also contributed to the formation of pores of the second one by sintering together. This way, the volume of pores associated with the surface of the type 1 pore is decreasing and the surface associated with the second type of pores is increasing. Having seen that the reactivity of the sample carbonation shows good correlation with the porosity of the first type, a model has been developed to predict the sorbent reactivity after a few cycles. This model, however, does not include the sample's residual activity, and in a later publication (Sun et al., 2008), the authors claim that some of the pores of the second type have also contributed to the reactivity of the sorbent. Unfortunately, this mechanism is difficult to apply in sintering of sorbents, characterised by monomodal pore distribution at the boundary between pores of the first and the second type, while during subsequent cycles, a bimodal pore size distribution is observed with the first type of pores, approaching the size of 85 nm, whereas the type 2 pore diameter is slowly increasing.

One of the solutions applied to modify sorbents is thermal pre-treatment. In their paper, Kotyczka-Moranska et al. (2011) provided a review of the known studies on the sorbent sintering. Another method of the Ca-based sorbent modification was presented in a paper by Yin et al. (2012). The authors examined reactivation of calcium based sorbents by means of ultrasounds. Application of ultrasounds during chemical reactions is referred to as sonochemistry. During the propagation of ultrasounds in a solution, microscopic bubbles filled with water vapour or gas are forming. In the next phase of the process, the bubbles implode, and this process is known as cavitation. During cavitation, "hot-spot" microareas, as they are referred to, may be formed, and the pressure inside them rises up to 500 bar and the temperature is up to 5,200 K. Ultrasounds within the frequency range of 100 kHz–1 MHz cause that average cavitation bubbles take part in sonochemical reactions. The greatest advantage of the ultrasound application is that the process can be conducted at room temperature in the presence of ultrasounds, even though the reaction normally takes place at high temperatures. Another method used in the aforementioned study for the sake of the

sorbent modification involved application of hydrochloric acid whose function was to increase the sorption capacity (expressed by an increase in the degree of carbonation). By binding calcium and magnesium in salts, the hydrochloric acid catalysed the cyclic reactions of carbonation and calcination.

The aim of this research was to modify natural calcium sorbents by different methods known from the literature, to determine their sorption parameters during the CO<sub>2</sub> capture process and to compare the methods analysed.

## Preparation of samples and experimental systems

The authors of this paper investigated natural Polish mineral sorbents and modified mineral sorbents: raw limestone from Czatkowice, heat-treated limestone from Czatkowice, chlorine-modified limestone from Czatkowice, limestone modified with ultrasounds and HCl from Czatkowice and dolomites from Siewierz.

Application of ultrasounds in a commercial technology generally requires that an additional ultrasonic reactor should be used and the reactivated sorbent should be cooled. The Siewierz dolomites studied were modified in two ways: by rinsing in hydrochloric acid and by using both rinsing and ultrasounds in order to increase the reaction velocity and efficiency. Two hydrochloric acid concentrations were applied: 0.1 and 0.2 mol/dm<sup>3</sup>. The sorbents were immersed in hydrochloric acid and a half of them was modified with ultrasounds for 1 minute. The Czatkowice limestone was modified with ultrasounds in a water bath for 1 minute. After the modification, sorbents were dried for 48 hours at the temperature of 40° C. All tests were conducted using the STA 409PG Luxx thermogravimetric analyser (by Netzsch). Samples with a mass of  $m_s = 10.0 \pm 0.1$  mg were placed in an Al<sub>2</sub>O<sub>3</sub> crucible. The measurements were conducted at 650° C (carbonation temperature) and 900° C (calcination temperature), with gas flow rates of 50 cm<sup>3</sup>/min and at the CO<sub>2</sub> concentration of 50%. SEM figures were obtained using the Nova NANOSEM 200 scanning electron microscope (by FEJ EUROPE). The mercury porosimetry was investigated by means of Autopore IV 9500. The sample was degassed in a vacuum bellows of 100 μm for 5 minutes.

## Results and discussion

### Physicochemical modification of sorbents

Results of our experiments have been presented in Fig. 1 and 2. Figure 1 shows a comparison of results of consecutive carbonation and calcination cycles for raw limestone from Czatkowice, modified by means of ultrasounds and chlorine. As shown, the sorbent modified with chlorine significantly contributes to the deterioration of its performance in successive cycles, and the sorbent reactivation with ultrasounds enhances its activity, but the ratio between the amount of CO<sub>2</sub> absorbed in the dynamic and the static part of the carbonation process is inferior compared to the raw material.

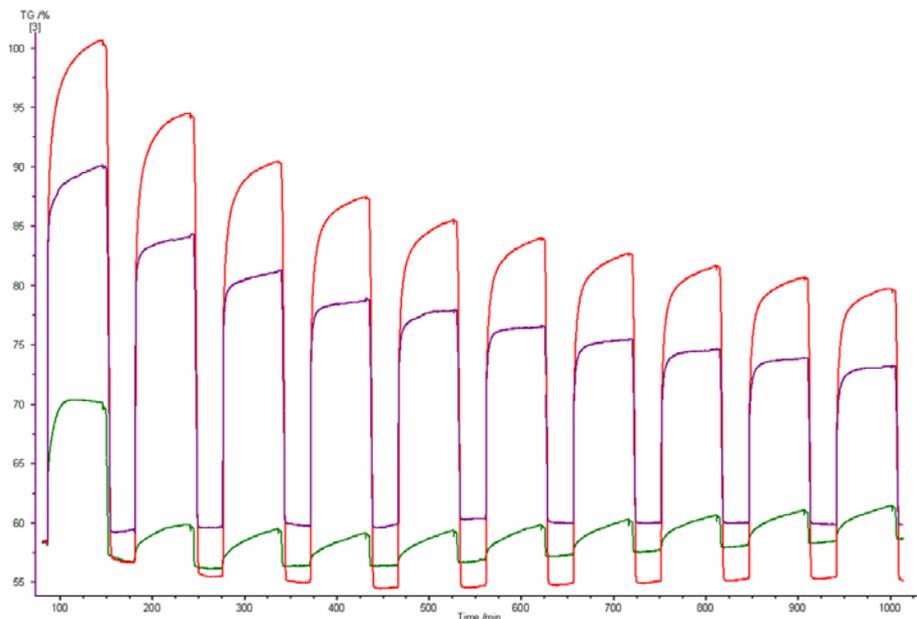


Fig. 1. Comparison of mass changes following the carbonation and calcination cycles for raw limestone from Czatkowice (red), ultrasound-modified limestone from Czatkowice (purple) and chlorine-modified limestone from Czatkowice (green)

Figure 2 illustrates a comparison of results of the consecutive carbonation and calcination cycles for the Siewierz dolomite modified with HCl in the presence of ultrasounds and that treated with HCl only. Both experiment configurations were conducted for two hydrochloric acid concentrations of 0.1 and 0.2 mol/dm<sup>3</sup>.

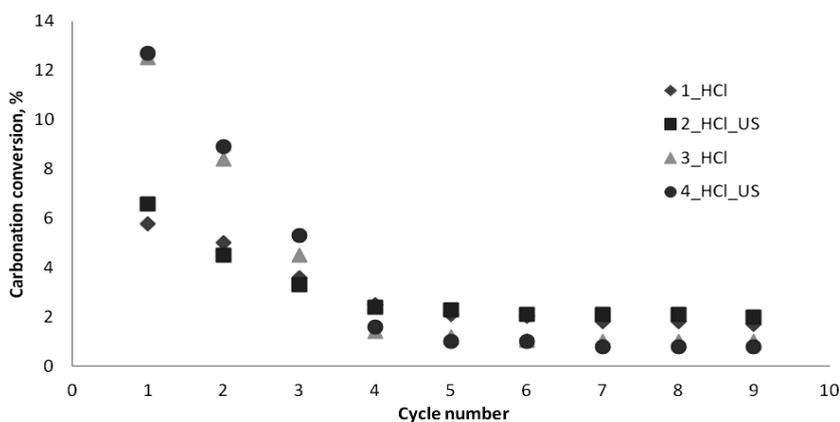


Fig. 2. Comparison of carbonation conversion degrees in consecutive carbonation and calcination cycles for dolomite from Siewierz modified with HCl and with HCl in the presence of ultrasounds (HCl\_US).

Series 1 and 2 were obtained for the hydrochloric acid concentration of 0.2 mol/dm<sup>3</sup> and series 3 and 4 for the concentration of 0.1 mol/dm<sup>3</sup>

The only result of applying the concentration of  $0.2 \text{ mol/dm}^3$  is a lower degree of carbonation in the first cycles. The approximate degree of carbonation of modified sorbents in three cycles is comparable. The application of ultrasounds did not significantly impact the ability to bind  $\text{CO}_2$  in the dolomite. No significant effect of the ultrasound application is probably due to the fact that the reaction between  $\text{HCl}$  and the sorbent is characterised by a very high velocity, thus the application of ultrasounds could not affect the increase in the acid penetration of the pores. However, the experimental results show no increase in the sorption capacity of the dolomite in subsequent cycles of the study.

### Thermal modification of sorbents

According to the recent knowledge, thermal heating of sorbents is yet another method of their modification. In our previous experiments, pre-sintering of natural sorbents at  $1000^\circ \text{C}$  resulted in a significant conversion drop in the first  $\text{CO}_2$ -capture reaction followed by enhancement throughout  $\sim 10$  cycles. As already discussed in the authors' previously published paper (Kotyczka-Moranska et al., 2011), the decrease in the carbonation conversion is probably associated with sintering of the sorbent's active surface. In this paper, the authors have presented results of the structure examinations for thermally pre-treated sorbents. Figs 4 and 5 illustrate the morphology of raw (A) and thermally modified sorbents (B).

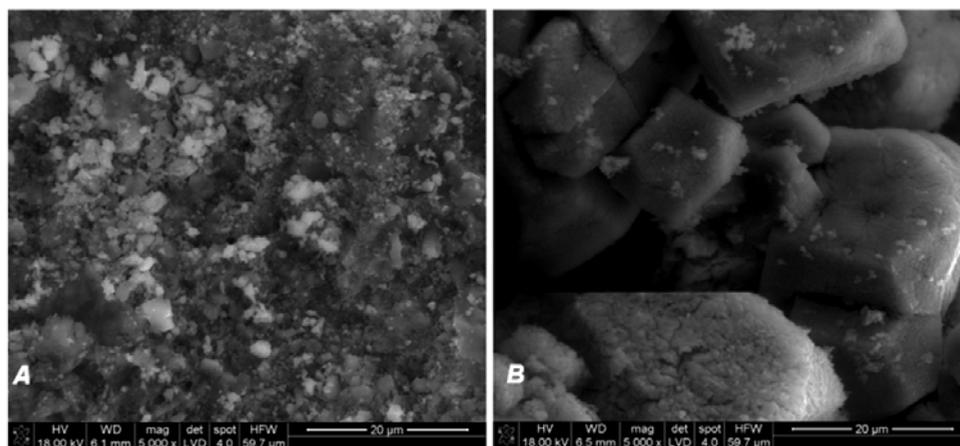


Fig. 3. SEM photo of raw (a) and thermally pre-treated (b) limestone

Manovic and Anthony (2008) have claimed that, after heating the sorbent, the surface is composed of large grains and pores of the order of  $1 \mu\text{m}$ . They have similar dimensions and smooth surfaces which mean that small pores have been eliminated by heating and consequently the number of large pores has increased. It is consistent with the SEM photos provided in Figs 3 and 4 as well as results of the mercury porosimetry (Fig. 5).

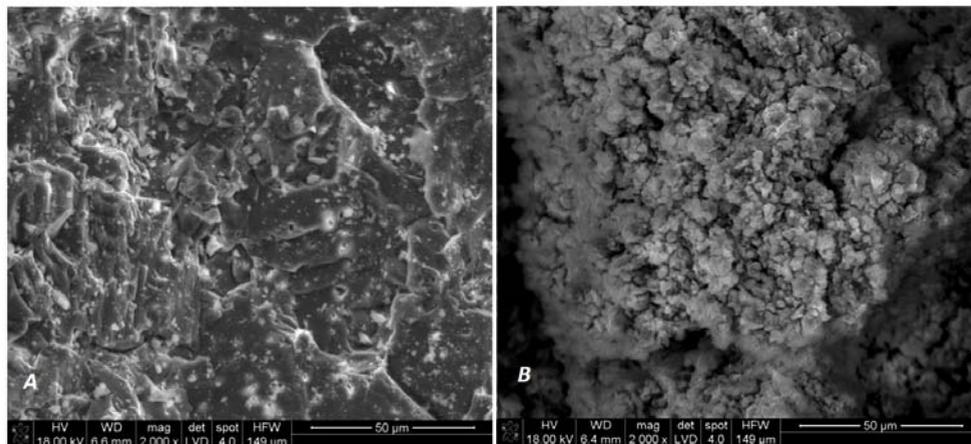


Fig. 4. SEM photos of raw (a) and thermally pre-treated (b) dolomite

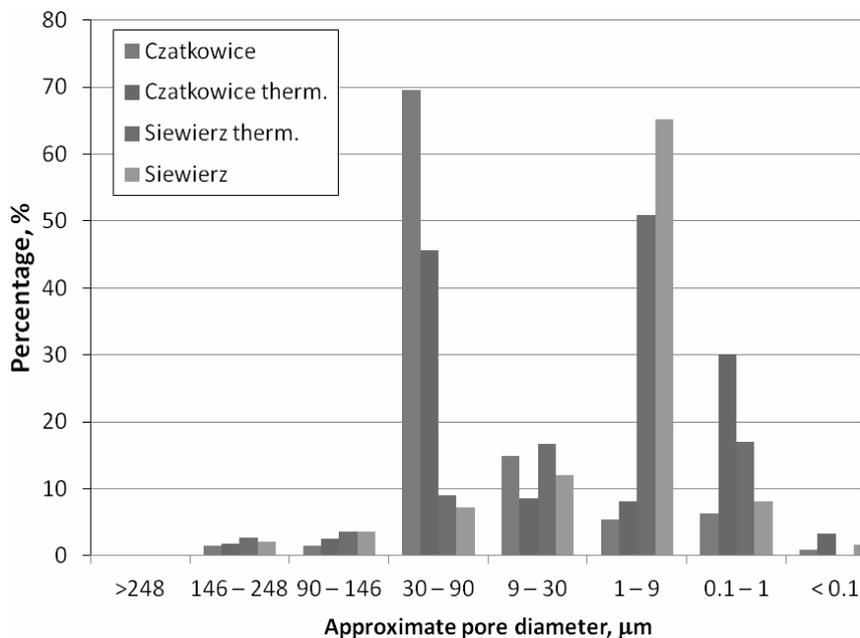


Fig. 5. Approximate pore diameter of the sorbents examined

Table 1 contains results of the mercury porosimetry testing of raw and sintered sorbents. One may clearly notice that, in both cases, the total pore area increases and the bulk density is reduced after the thermal pre-treatment for the Czatkowice limestone and the Siewierz dolomite examined. The median pore diameter clearly increases slightly for the Czatkowice limestone and the Siewierz dolomite as well.

Table 1. Results of porosimetry testing of raw and sintered sorbents

Parameter	Unit	Sorbent tested			
		Czatkowice	Czatkowice therm.	Siewierz	Siewierz therm.
Total Intrusion Volume	cm <sup>3</sup> /g	0.2889	0.9239	0.3173	0.6376
Total Pore Area	m <sup>2</sup> /g	0.476	7.917	1.042	1.724
Median Pore Diameter (Volume)	µm	24.73	30.13	4.15	5.86
Bulk Density at 0.43 psia	g/cm <sup>3</sup>	1.50	0.73	1.41	1.01
Apparent (skeletal) Density	g/cm <sup>3</sup>	2.66	2.24	2.57	2.83
Porosity	%	43.48	67.47	44.93	64.36

Unfortunately, based on results provided, it is difficult to state what the exact amount of type 1 pores is. Because of that, one can only infer conclusions about the changes to the pore structure of the sorbents tested from the fluctuations in the number of pores of the second type. As for the raw limestone sorbent from Czatkowice, the number of pores of less than 1 µm in size was smaller than in preheated sorbent. In the case of preheated limestone, there was a significant increase in the number of pores in the category of less than 1 µm, which may suggest an inclination towards monomodal distribution of pores at the boundary between pores of the first and the second type. This conclusion is supported by a drastic decrease in the activeness of the preheated sorbent (Kotyczka-Moranska et al., 2011).

## Conclusions

The purpose of the authors' study was to determine the best way to modify mineral CO<sub>2</sub> sorbents for calcium looping processes. Taking the results presented into consideration, one may claim that the most interesting modification method is the application of ultrasounds. All attempts to modify the sorption parameter of sorbents by applying chlorine have failed. A thorough analysis has led the authors to a conclusion that chlorine salts do not perform the function of a framework in modified sorbents. This phenomenon occurred in both the sorbents studied, i.e. limestone and dolomite. The next step in the research will be testing of the influence ultrasounds exert on parameters of sorbents. This paper also provides a discussion on the effects of preheating on the morphology of sorbents. One may notice that the results provided reflect the phenomenon known from the literature, i.e. sintering of pores on the surface of sorbents.

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