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## APPLICATION OF POLISH CALCIUM SORBENTS IN CARBONATE LOOPING

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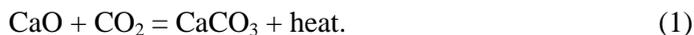
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**Abstract:** The purpose of this work was the investigation of behaviour of three Polish CaO-based sorbents during calcium looping cycles. All investigations were conducted with a Netzsch STA 409PG Luxx thermogravimetric analyser. Samples weighing  $m_s = 10.0(1)$  mg were placed in an  $Al_2O_3$  crucible. The calcium looping processes were performed at two carbonation temperatures (650°C and 680°C) and three calcination temperatures (880°, 900° and 920°C). Additionally, calcination-carbonation cycles with different gas flows were explored. We investigated the influence of  $CO_2$  concentration and total gas flow on carbonation conversion.

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

### Introduction

The emission of  $CO_2$  from fossil fuel combustion is the major contributor to anthropogenic greenhouse gas emissions. During the last several years, CaO-based sorbents have been intensively investigated for their possible applications in  $CO_2$  capture. Among the various options for the separation of  $CO_2$  from flue gases, high-temperature  $CO_2$  absorption by mineral sorbents such as Ca-sorbents appears promising. The main reaction in this process is the carbonation reaction:



The sorbent can be regenerated via calcination, which entails heating the carbonate until it decomposes into CaO and  $CO_2$ . In this process, pure  $CO_2$  is obtained for sequestration. The regenerated sorbent can then undergo another round of carbonation. This process is based on a looping cycle in which the two reactions, carbonation and calcination, are alternated. The carbonation reaction is exothermic, whereas calcination reaction is endothermic. Carbonation is characterised by a rapid initial rate and a very slow final reaction rate. Calcination is a rapid process that occurs over a wide

temperature range (Blamey et al., 2010). Thus, the carrying capacity of the sorbent is the number of moles of  $\text{CO}_2$  reacted in the period of fast reaction rate with respect to that of the reaction stoichiometry for complete conversion of  $\text{CaO}$  to  $\text{CaCO}_3$ . The main disadvantage of  $\text{CaO}$ -based sorbents is the decay of activity with an increasing number of cycles. This decay trend was summarised by Abanades and Alvarez (2003) as the following first-order formula:

$$X_N = f_m^N (1 - f_w) + f_w \quad (2)$$

where  $X_N$  is the carbonation conversion in the  $N$ th cycle, and  $f_m$  and  $f_w$  are empirical parameters.

The optimal values of these parameters were calculated from a data series found in the literature as  $f_m = 0.77$  and  $f_w = 0.17$ . This equation was fitted to carbonation/calcination data from over 50 cycles, and an excellent regression coefficient of approximately 0.99 was obtained, indicating that fresh sorbent is needed in the calcium looping process due to its deactivation, which increases the cost of the process. For this reason, it is necessary to mitigate natural sorbent deactivation (Li, 2011). The largest deviation from the optimum value given by equation 2 is found in processes where in a considerable sintering was observed, and the deactivation rate of the sorbents increased accordingly. Fennell et al. (2007) found that equation 2 does not describe sorbent activity in a fluidised bed environment because increasing the calcination period reduces  $f_m$ . This parameter can be interpreted as a residual reactivity. Mess et al. (1999) observed that sorbent particles remained capable of forming a  $\text{CaCO}_3$  layer despite undergoing numerous cycles. For this reason, the term  $f_m$  and equation 2 are more applicable in systems where attrition and friability are less significant. An alternative formula was developed by Wang and Anthony for carbonation conversion activity (Wang and Anthony, 2005):

$$a_N = a_{N-1} (1 - ka_{N-1}) \quad (3)$$

where  $k$  is a proportionality coefficient, and  $a_N$  is the activity of the sorbent in the  $N$ th cycle.

These authors reported that activity decay depends on the activity of the sorbent in the  $(N - 1)$  cycle. Their formula describes the data quite well with  $k = 0.23$ . The disadvantage of this formula is its limitation in  $N$ , becoming useless when  $N$  is large. As an alternative for large  $N$ , Wang and Anthony (2005) proposed equation (4):

$$a_N = \frac{1}{1 + kN} \quad (4)$$

In this equation, the parameter  $k$  is the rate of decay of sorbent activity. This equation is reminiscent of the formula for catalyst deactivation by sintering as function of time  $t$ :

$$a_N = \frac{1}{1 + kt} \quad (5)$$

Equation (5) suggests that sintering is the cause of decay. The equation proposed by Wang and Anthony does not include residual reactivity. Grasa and Abanades (2006) developed Eq. 4 to account for the residual activity:

$$a_N = \left[ \frac{1}{\frac{1}{1 - a_\infty} + kN} + a_\infty \right] \times 100 \quad (6)$$

where  $a_\infty$  is the residual activity, with a value of approximately 7%.

This equation is useful for data for up to approximately 500 cycles, where  $a_\infty = 0.075$ . Another formula was subsequently proposed by Lysikov et al. (2007):

$$a_N = \left[ \frac{1 - a_\infty}{(1 + kN)^\alpha} + a_\infty \right] \times 100 \quad (7)$$

where  $a_\infty$  is the residual activity, and  $\alpha$  is a parameter that depends on the sintering mechanism. This formula is especially useful for synthetic sorbents but requires an additional parameter  $\alpha$ . Wang and Anthony (2007) later proposed a formula that includes residual reactivity:

$$a_N = a_{N-1} [1 - k(a_{N-1} - a_\infty)] \times 100 \quad (8)$$

which, for large number of cycles, reduces to the following:

$$a_N = \left[ \frac{a_\infty}{1 - (1 - a_\infty)e^{-ka_\infty N}} \right] \times 100 \quad (9)$$

This equation also describes decay behaviour in systems where sintering occurs. There are numerous equations in the literature that can fit experimental data, but there is no ready correlation between their parameters, sorbent characteristic and process conditions. Therefore, the final sorbent capacity after an “infinite” number of cycles is not predictable. This situation demonstrates that the influence of different process parameters on sorbent activity requires additional investigation. Manovic and Anthony (2008) examined the influence of temperature on sorbent activity using the same temperatures for calcination and carbonation and found that sorbent sintering is masked at higher temperatures by enhanced carbonation due to increased CO<sub>2</sub> diffusion through the CaCO<sub>3</sub> layer. These authors concluded that a long carbonation period led to a faster loss of sorbent activity and further showed that a longer calcination period

increases sorbent conversion. Their results stand in contrast to those presented by Grasa and Abanades (2006) and Lysikov (2007), who reported that calcination time is not an important parameter.

The aim of this work was to determine the carbonation/calcination process parameters that allow for the most efficient use of the sorbent in a calcium looping installation. For this purpose, we studied the influence on sorbent activity of parameters such as carbonation and calcination temperatures, the  $\text{CO}_2/\text{CaO}$  ratio in the reactor and the choice of mineral sorbent.

## Experimental system

We investigated three natural Polish mineral sorbents: limestone from Czatkowice and dolomites from Siewierz and Sandomierz. All investigations were conducted in an STA 409PG Luxx thermogravimetric analyser (Netzsch). Samples of mass  $m_s = 10.0(1)$  mg were placed in an  $\text{Al}_2\text{O}_3$  crucible. The measurements were conducted at various carbonation and calcination temperatures, gas flows and  $\text{CO}_2$  concentrations.

## Results and discussion

Figure 1 presents a comparison of these three mineral sorbents during ten calcination/carbonation cycles.

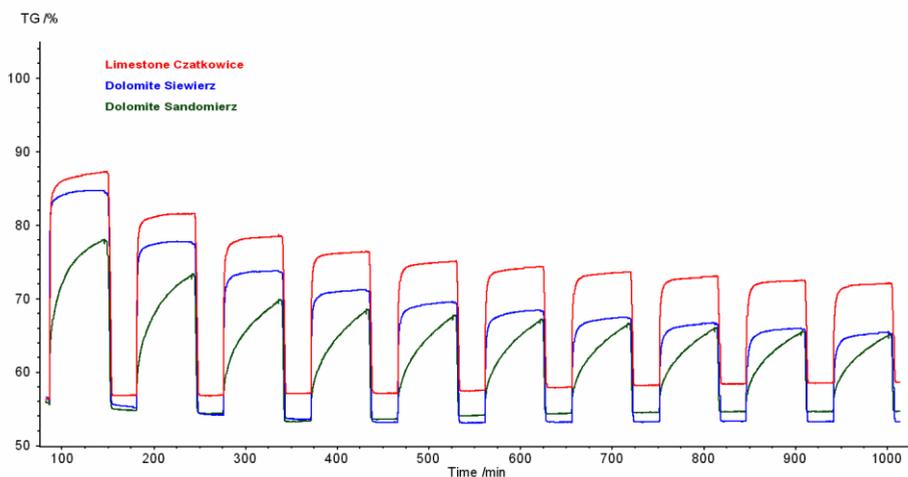


Fig. 1. Comparison of three mineral sorbents during ten calcination/carbonation cycles

All the measurements were conducted under the same conditions: carbonation at  $650^\circ\text{C}$ , calcination at  $900^\circ\text{C}$  and a  $\text{CO}_2$  flow of  $25 \text{ cm}^3/\text{min}$  during carbonation. The simple comparison of the two dolomites shows that the dolomite from Sandomierz

displays worse sorbent properties because the period of fast reaction rate during the carbonation process is less than that of the dolomite from Siewierz. Therefore, we used the dolomite from Siewierz and the limestone from Czatkowice in our subsequent investigations.

The first stage of our measurements involved conducting carbonation/calcination cycles at different carbonation temperatures. We investigated two temperatures: 650°C and 680°C. These temperatures were chosen because their application in a calcium looping installation can be economically justified. Furthermore, we chose not to apply a higher temperature during carbonation to prevent sorbent sintering (Manovic and Anthony, 2008). Figure 2 presents the results for the limestone from Czatkowice. The calcination temperature was 900°C, and the gas flows consisted of 25 cm<sup>3</sup>/min CO<sub>2</sub> plus 25 cm<sup>3</sup>/min N<sub>2</sub> during carbonation and 25ml/min N<sub>2</sub> during calcination. We observed no difference between the results for this sorbent at these two temperatures.

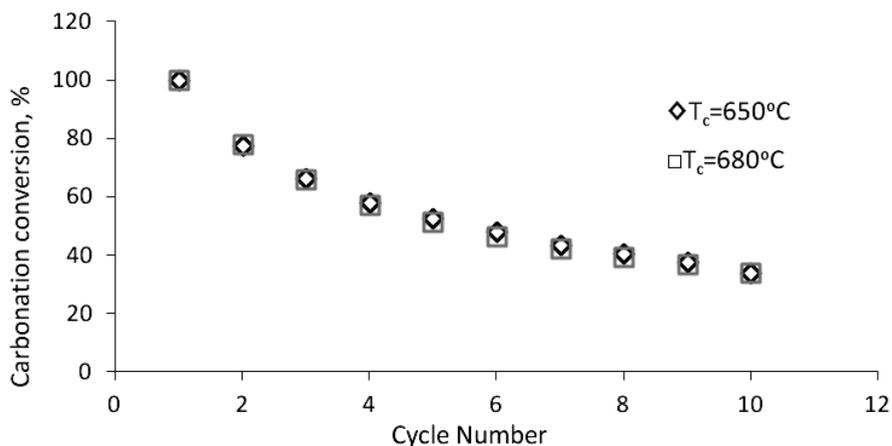


Fig. 2. Comparison of carbonation conversion of limestone for two carbonation temperatures

The second part of our study consisted of investigating the influence of calcination temperature on sorbent activity. For the limestone, we compared three calcination temperatures: 880, 900 and 920°C. The cycles were performed at a carbonation temperature of 650°C and the gas mixtures consisted of 25 cm<sup>3</sup>/min CO<sub>2</sub> plus 25 cm<sup>3</sup>/min N<sub>2</sub> during carbonation and 25 cm<sup>3</sup>/min N<sub>2</sub> during calcination.

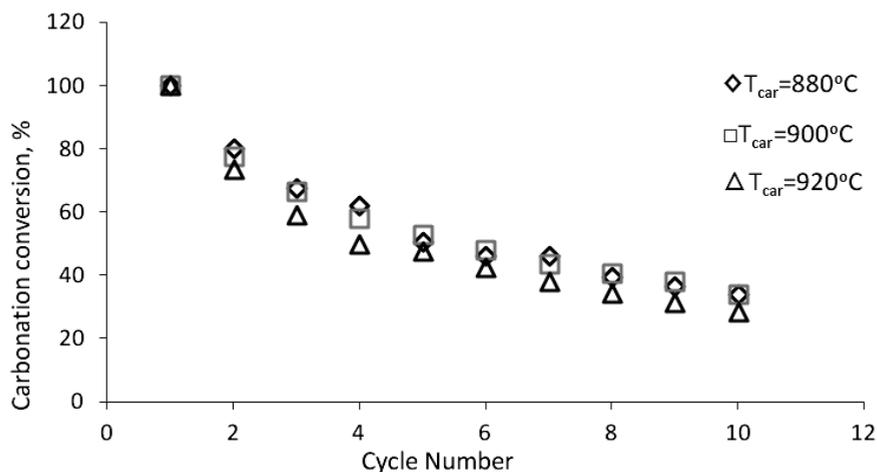


Fig. 3. Comparison of the carbonation conversion of limestone at three calcination temperatures

Figure 3 presents a comparison of the carbonation conversion for limestone at the three studied temperatures. There was no difference observed between carbonation conversions at 880°C and 900°C, but carbonation conversion was lower at 920°C. These results are in accordance with the results presented by Manovic and Anthony (2008), who reported that samples cycled at higher temperature were more sintered and, hence, less active. However, the calcination temperature in an industrial reactor should be at least 900°C to achieve calcination yielding a concentrated CO<sub>2</sub> stream. Thus, it appears appropriate to conduct further investigations at a calcination temperature of 900°C and a carbonation temperature of 650°C. The second investigated sorbent was the dolomite from Siewierz. We conducted measurements in the same way as for the limestone, and the results were the same as for the limestone. Regarding the first variable (carbonation temperature), there was no difference between the results obtained with carbonations at 650°C and 680°C. In processes with different calcination temperatures, the results were also similar to the limestone results. The worst carbonation conversion was obtained for calcination conducted at 920°C.

The last part of our investigation consisted of calcination/carbonation processes conducted using several different gas flows with various CO<sub>2</sub> concentrations. These measurements were all conducted at a calcination temperature of 900°C and a carbonation temperature of 650°C.

Figure 4 presents the data obtained in four limestone calcination/carbonation cycles conducted with four different gas flows during carbonation (24, 50, 100 or 150 ml/min) with a constant CO<sub>2</sub> concentration (50%). The partial gas flows are also presented in this figure. Nitrogen was used as a purge gas at a constant flow rate in each process (12, 25, 50, or 75 cm<sup>3</sup>/min). We observed that the carbonation conversion is better at lower gas flows than with the largest gas flow (150 cm<sup>3</sup>/min). The influence of CO<sub>2</sub> concentration on carbonation conversion was also investigated. Three process-

es with different CO<sub>2</sub> concentrations (25, 50 or 75%) but a constant total gas flow during carbonation (100 cm<sup>3</sup>/min) were evaluated with the limestone.

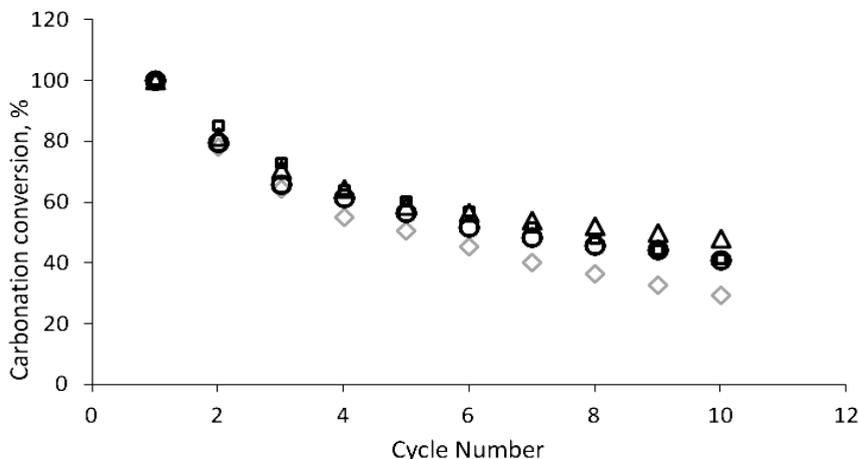


Fig. 4. Comparison of carbonation conversion of limestone for four gas flows:

◇ – N<sub>2</sub> 75 cm<sup>3</sup>/min/CO<sub>2</sub> 75 cm<sup>3</sup>/min; □ – N<sub>2</sub> 50 cm<sup>3</sup>/min/CO<sub>2</sub> 50 cm<sup>3</sup>/min;  
 △ – N<sub>2</sub> 25 cm<sup>3</sup>/min/CO<sub>2</sub> 25 cm<sup>3</sup>/min; ○ – N<sub>2</sub> 12 cm<sup>3</sup>/min/CO<sub>2</sub> 12 cm<sup>3</sup>/min

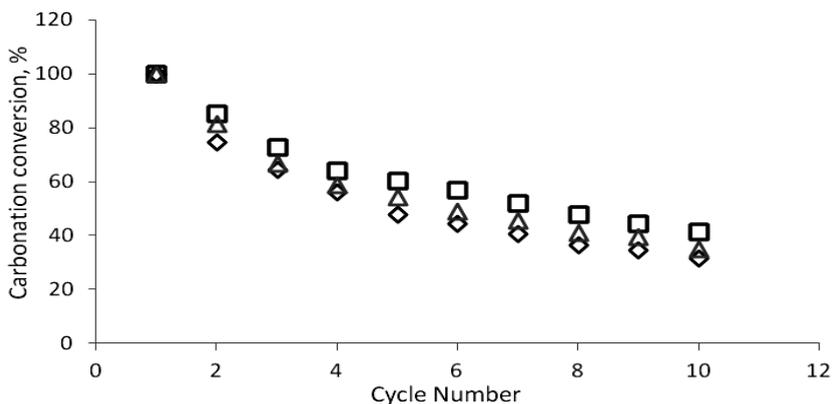


Fig. 5. Comparison of carbonation conversion of limestone for three CO<sub>2</sub> concentrations with the same gas flow: ◇ – N<sub>2</sub> 25 cm<sup>3</sup>/min/CO<sub>2</sub> 75 cm<sup>3</sup>/min; □ – N<sub>2</sub> 50 cm<sup>3</sup>/min/CO<sub>2</sub> 50 cm<sup>3</sup>/min;  
 △ – N<sub>2</sub> 25 cm<sup>3</sup>/min/CO<sub>2</sub> 75 cm<sup>3</sup>/min

The data presented in Fig. 5 show that the carbonation conversion is slightly lower at 75% CO<sub>2</sub> than at the other CO<sub>2</sub> concentrations. This result may be related to the fact that an atmosphere of concentrated CO<sub>2</sub> also amplifies sintering, consequently reducing the sorbent activity with an increasing number of reaction cycles. This phenomenon can also be observed in Fig. 6.

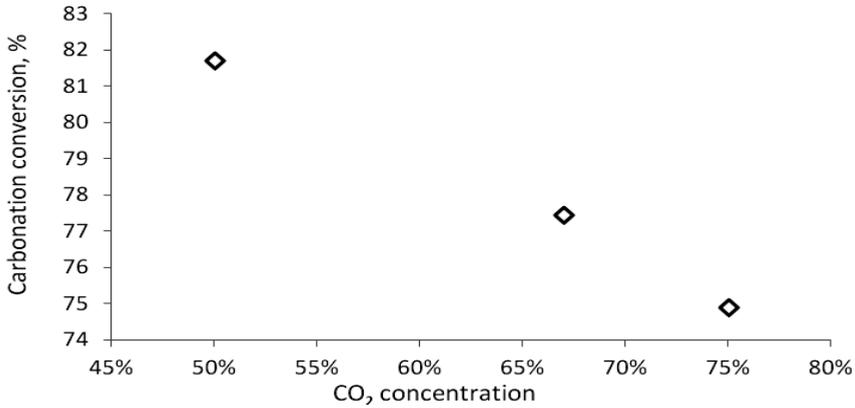


Fig. 6. Carbonation conversion of limestone for three CO<sub>2</sub> concentrations (purge gas flow 25 cm<sup>3</sup>/min)

This graph presents the relation between CO<sub>2</sub> concentration and carbonation conversion during the first cycle. In these processes, the purge gas flow was constant (25 cm<sup>3</sup>/min), and CO<sub>2</sub> concentration was varied (50, 67 and 75%). The same types of measurements were performed for the dolomite, and in both cases (constant CO<sub>2</sub> concentration and constant total gas flow), there were no differences between the data obtained. Figure 7 presents the data collected at a constant total gas flow; here, it can be observed that dolomite activity does not depend on CO<sub>2</sub> concentration in this range.

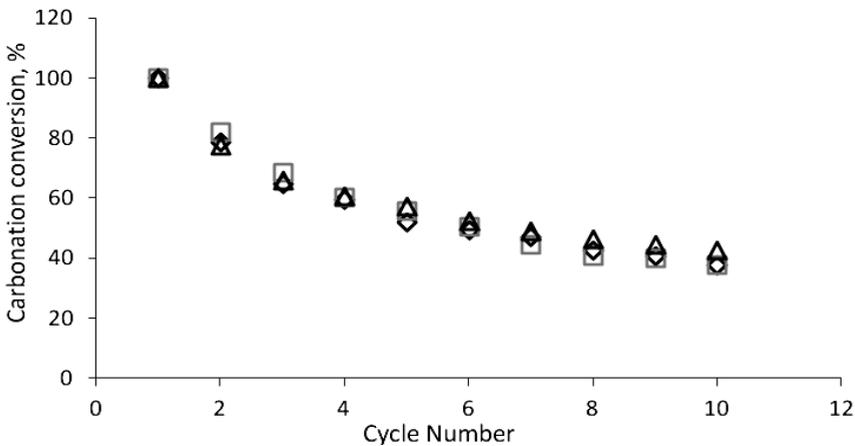


Fig. 7. Comparison of carbonation conversion of dolomite for three CO<sub>2</sub> concentrations with the same gas flow: ◇ – N<sub>2</sub> 25 cm<sup>3</sup>/min/CO<sub>2</sub> 75 cm<sup>3</sup>/min; □ – N<sub>2</sub> 50 cm<sup>3</sup>/min/CO<sub>2</sub> 50 cm<sup>3</sup>/min; △ – N<sub>2</sub> 25 cm<sup>3</sup>/min/CO<sub>2</sub> 75 cm<sup>3</sup>/min

Because the CO<sub>2</sub> concentration in typical flue gas is approximately 20%, we decided that the best data for further analysis were those obtained at 20% CO<sub>2</sub>. Figure 8

presents a comparison of our data for limestone and dolomite in 10 carbonation/calcination cycles with three curves representing relations found in the literature (Eqs (2), (3), (8)). We observed that the activity of dolomite is slightly higher than that of limestone. All these equations describe carbonation conversion for limestone. As stated in the introduction, Eq. 2 does not consider sorbent sintering, and this equation did not describe our data. Furthermore, the equation developed by Wang and Anthony (Eq. (3); 2005) did not describe our data, but after the introduction of the factor for residual reactivity (Eq. (8)), corresponded to our data quite well.

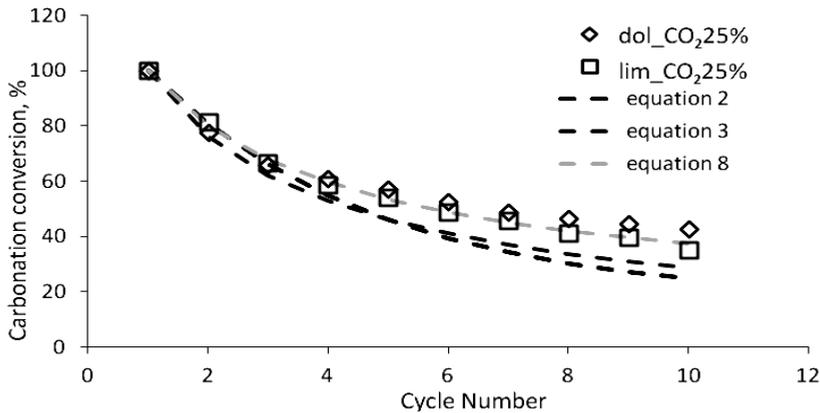


Fig. 8. Comparison of data obtained for limestone and dolomite in 10 carbonation/calcination cycles with the relations found in the literature

## Conclusions

The purpose of our work was to determine the best parameters for calcium looping processes conducted with Polish mineral sorbents. We investigated three mineral sorbents: one limestone and two types of dolomite. We excluded one type of dolomite early in our experiments due to its weak carbonation conversion. The two other sorbents were investigated at various carbonation and calcination temperatures and at different CO<sub>2</sub> concentrations and gas flows. We found that the best process parameters for our sorbents are a calcination temperature of 900°C and a carbonation temperature of 650°C. Additionally, we observed that there was no difference in carbonation conversion for dolomite in the range 25–75% CO<sub>2</sub>, and higher activity decay occurs with limestone at high CO<sub>2</sub> concentrations. We also found that the activity decay of the limestone from Czatkowice is well described by the equation developed by Wang and Anthony (Eq. 8). This relation is useful because it allows for the calculation of sorbent activity in a calcium looping installation after  $N$  cycles.

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