

Dolomites as Promising Natural CaO-based Sorbents for Ca-Looping Cycle CO₂ Capture

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September 2017

Abstract

The work presented in this article is in the scope of an ongoing research project “CaReCI - Carbon Footprint Reduction in Cement Industry” carried out at Instituto Superior Técnico in Lisbon, Portugal, in collaboration with CIMPOR (Cimentos de Portugal), which is the largest Portuguese Cement Industry.

Dolomites (CaMg(CO₃)₂) are commonly available in nature and it has been reported that calcined dolomite becomes a more efficient sorbent than calcined limestone for CO₂ capture by Ca-Looping. Therefore, natural dolomites could be used to produce promising cost-effective and eco-friendly improved CaO-based sorbents for industrial CO₂ capture applications. In this work, two dolomite samples were tested in an experimental unit lab scale fixed bed reactor and were characterized by the characterization techniques: X-ray diffraction (XRD), N₂ sorption, Thermogravimetric analysis (TGA) and Scanning Electron Microscope (SEM). The CO₂ capture capacity and stability along the cycles of carbonation-calcination of the dolomite samples were studied under different thermal pre-treatment atmospheres and with a carbonation gas feed composition of 15% and 25%.

The results showed that pre-calcination with CO₂ improves the sorbents carrying capacity and stability when compared with pure N₂ atmosphere.

The best results were obtained with dolomite pre-calcined with 25% of CO₂. The gas feed CO₂ composition during carbonation was not so relevant. The results are promising because they show that dolomites can be used as Ca-looping sorbents for CO₂ capture in power plants which flue gases CO₂ concentration is around 10-15% and in the cement industry where flue gases CO₂ concentration is around 25-30%.

Keywords: calcium looping, carbon capture and storage, CO₂ capture, dolomite, natural sorbent

1. Introduction

Nowadays due to the climate change, engineers, scientists and policy makers are looking for the solution to reduce the greenhouses gasses emissions (GHG), which has been priority for developed countries. The main reason of fast growth of global CO₂ emission in atmosphere is the combustion of fossil fuels and chemical processes in cement manufacture [1].

European Commission presented the strategy which introduced that there will be significant impact of implementation of low carbon technologies – CCS in the electricity mix.

The main goal is to reduce the amount of CO₂ in the flue gases. It is estimated that the share of CCS will increase around 60% in 2020, 80% in 2030 and 100% in 2050. The CCS technologies will improve the idea of transition to low carbon-based economy [2].

There are many types of CCS technologies. One of the most interesting is Calcium Looping Cycle which uses calcium based sorbents in the post-combustion technology. There are natural and synthetic sorbents which can be implemented in large stationary sources such as power plant or cement industry.

Technology of CO₂ capture can significantly contribute to reduce greenhouse gases effect. In a large application, cost is considered before implementation any of the CCS technologies. Post-combustion is an expensive technology but the implementation of the natural sorbents can significantly reduce its costs. However, main drawbacks are related with the fast deactivation of the sorbent to capture more CO₂ and sintering phenomena. To overcome this challenge, scientists are working on improvements of the sorbent ability to uptake more CO₂ [3].

Using sorbents in the post-combustion carbon capture technology has many advantages such as: [4]

- low costs of natural solid sorbents, allow to use them in high quantities in the system,
- they can be possible viable solution to limit CO₂ emissions;

- solid sorbents require less energy in the regeneration process compared to aqueous amines;
- they can be easily transported and send to the power plant;
- high capacity to capture CO₂, (this property is different and depends on type of the sorbent)

Table 1 presents the comparison between chosen sorbents used for CO₂ separation processes.

Table 1 List of chosen sorbents/solvents used for CO₂ capture in Power Plants [4]

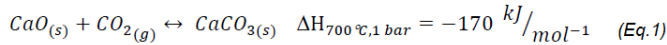
Sorbent/solvent material	Carrying capacity (gCO ₂ /kgsorbent/solvent material)
CaO oxides (assume 50% repeatable cycles)	393
Activated Carbon	88
Silica gel	13
MEA solvent	60

Chemical Looping is a promising CCS technology, due to its ability to capture CO₂ during coal gasification and large industrial scale post-combustion scale processes. It can be implemented in cement manufacture, steel and fossil-fired power plants. After the combustion of fuel, products such as CO₂ and H₂O are separated from flue gases. The method uses solid sorbents which contain metal oxide such as calcium (Ca) to capture CO₂ from flue gases [5]. It has many advantages; the most important ones are high capture capacity and possibility of sorbent's regeneration. The biggest challenge in the Ca-Looping is the choice of metal oxide which should be resistant to long cycling and other conditions which are present during combustion of fuel such as temperature [6].

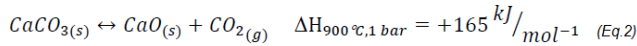
Flue gases containing CO₂ enter a carbonator, where solid sorbent (with CaO) is ready to capture CO₂ through carbonation reaction. During the calcination, CaCO₃ decomposes into CaO and CO₂ at temperature between 800 °C and 900 °C. CaO is sent

to the carbonator where cycle (calcination and carbonation) is repeated [7]. From the calciner, CO₂ is compressed and utilized or stored. CCU (Carbon dioxide utilisation) enables to convert CO₂ to valuable products. By direct utilisation, many products as: bio-oils, chemicals, and fuels can be obtained.

The most significant reaction in Ca-Looping is carbonation (Eq.1), where CaO reacts with CO₂ to obtain calcium carbonate CaCO₃ as it is given by the equation:



Obtained CaCO₃ goes to calciner where it decomposes into CaO. Then it is sent again to carbonator and finally, the chemical loop cycle is completed. Calcination reaction is presented below (Eq.2):



Two main reversible reactions of calcination and carbonation are different and at this point, it is important to observe the graph of relationship between vapor pressure and temperature, which is shown in Figure 1. Carbonation depends on the temperature and pressure of its vessel. The reaction is carried out at temperatures higher than 870 K (596.85 °C) under high CO₂ partial pressures which aim to produce pure stream. Therefore, in the carbonator vessel, the temperature is lower and it enables to regenerate the sorbent capacity, in order to reuse the sorbent in the next cycle to capture CO₂.

The calcination temperature depends on the CO₂ pressures, given by the (Eq.3):[8]

$$\log_{10} P_{eq} (\text{atm}) = 7.079 - \frac{8308}{T} (K) \quad (\text{Eq.3})$$

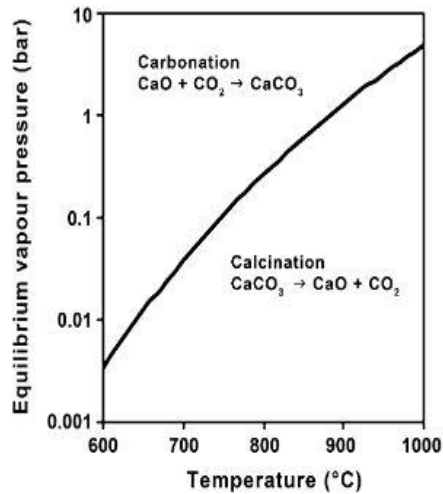
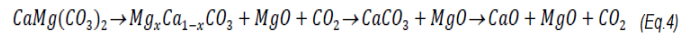


Figure 1 Equilibrium vapour pressure of CO₂ over CaO as a function of temperature (adapted from [9])

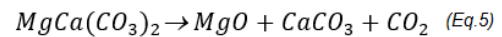
There are two known Calcium Looping pilot scale plants which are implemented in the industrial sector. The most known is European project–CaOling which is integrated with coal power plant. The second largest installation is High-efficiency Calcium Looping Technology (HECLOT), which is in Taiwan and collaborates with Cement Industry [10]. It was estimated that “Cement factories emit between 0.6-1 kg of CO₂ per 1 tonne of cement” (ECRA 2007), justifies the implementation of CCS or CCU [11].

There are natural and synthetic sorbents. They both can be used to capture CO₂ in the cement industry process [12]. Natural carbonate rocks used in the chemical looping technology are waste marble powder (WMP), limestone, and dolomite. Less common are egg shells and sea shells [13]. These materials can be crushed to powder and then used as sorbents in many industrial processes.

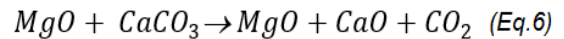
Other important and available sorbent in natural environment is dolomite which chemical formula is (CaMg(CO₃)₂). The percentage of oxides depends on the composition of the dolomite. Recently, scientists conducted more research on dolomite. Due to the chemical composition and availability of magnesium in its structure, the conditions of carbonation and calcination are different [14]. It was verified that capture capacity of the dolomite is lower than that of limestone. However, its reactivity among the cycles lasts longer. The main reason is less sintering compared to limestone and that MgO in dolomite doesn't capture CO₂ [15]. The ratio of CaO/MgO has major influence on CO₂ capture behavior by the sorbent. During the calcination process, MgCO₃ decomposes contributing to improvement of CO₂ compound to enter into particles by an increase in surface area and pore volume [16]. In a pure CO₂ atmosphere, dolomite decomposes as given by (Eq.4) [16]:



As shown in the above equation, the intermediate, unstable compound, Mg_xCa_{1-x}CO₃ appears as dolomite is composed of MgCO₃. Generally, decomposition depends on the percentage amount of oxides which can be formed based on the chemical formula. The calcination of MgCO₃ occurs at lower temperature so it decomposes before that CaCO₃ [16]. It is given by (Eq.5):



The obtained product is partially calcinated, and when temperature increases, complete calcination of the dolomite occurs. It occurs due to the reaction between MgO and CaCO₃ causing an increase in pore volume and porosity of the sorbent [16]. The complete calcination reaction is given by the (Eq.6):



2. Materials and Methods

The dolomites studied are from a production plant in Turkey and have the commercial names: Omyadol 5-GZ and Omyadol SF-GZ. For simplicity, these dolomite samples will be called as dolomite α and dolomite β, respectively. Both types are obtained from high purity of white dolomite and contain calcium magnesium carbonate. The table 2 presents the data regarding the particle sizes for both dolomites. Dolomite β is more finely powdered compared to dolomite α.

Commercial MgO sample from Merck was also tested (99.9% of purity). To guarantee that all the sorbent samples don't have any moisture, the samples were dried and maintained at 120°C in the oven before the experimental tests.

The sorbents were characterized by the following techniques: N₂ sorption, X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Both dolomite samples were experimentally tested for assessing their CO₂ carrying capacity in a fixed bed reactor.

Table 2 The specific product data for dolomite α and dolomite β (adapted from company specific product data: Omya Madencilik)

Fineness Parameters (particle size distribution, % by weight)	Dolomite α	Dolomite β
Top cut (d98%)	28 μm	9 μm
Mean particle size (d50%)	6 μm	2.5 μm
Particles <2μm	23%	40%

The elemental composition was carried out in the Laboratory of Analysis in IST (LAIST). The elements like: Ca, Mg, Al, Si and Fe were analysed by ISO 11885:2007 and the C was analysed by an

internal method that is accredited by IPAC (Portuguese Institute of Accreditation). The elemental composition (Table 3). is important to calculate the capacity of sorbents to capture CO₂ among the cycles. The general chemical formula for dolomite is CaMg(CO₃)₂.

Table 3 includes the data of the chemical composition of dolomite α and dolomite β. Based on data in the table 3, it can be concluded that dolomite α has slightly less amount of calcium (Ca) than dolomite β, but a little more magnesium (Mg) in its composition. That small differences between them can influence the carrying capacity to capture CO₂ among the cycles. Besides the main elements which will be considered, the dolomite contains another elements which are treated as impurities like silicon (Si), aluminium (Al) and iron (Fe).

Table 3 Chemical elemental analysis of dolomites

Fresh sorbent	Elemental Content (%)					
	Si	Ca	Mg	Al	Fe	C
Dolomite α	0.05	24.0	11.7	0.02	0.02	12.8
Dolomite β	0.04	24.9	10.2	0.01	0.01	12.6

3. Experimental planning

The main aim of the experimental tests is to test dolomite samples for determining which could be successfully implemented in a pilot scale Calcium Looping technology. For this purpose, the experimental work was performed in two steps:

Step 1. Comparison of CO₂ carrying capacities of the two dolomites

Step 2. Effect of pre-calcination and carbonation atmospheres in CO₂ carrying capacity and stability of the selected dolomite sample.

In both steps it was performed a systematic study of the textural (N₂ sorption), mineralogical (XRD) and morphological (SEM) properties of the fresh and used sorbents. To understand the deactivation of sorbents along the cycles, were performed experimental calcination-carbonation tests with different number of cycles. For comparison purposes, the same pre-calcination conditions (100% of N₂) were applied during the comparison of two dolomites. The dolomite with higher CO₂ carrying capacity was chosen to be studied in step 2. The table 4 summarizes the tests carried with both dolomites.

Table 4 Summary of the tests carried out in the fixed bed unit

Pre-calcination atmosphere	Dolomite α	Dolomite β
100 % N ₂	0 Cycles	
	5 Cycles	
	10 Cycles	
	20 Cycles	

In the second step of the experimental planning, it was assessed the effect of different pre-calcinations (CO₂, N₂) and the effect of use different percentages of CO₂ during the carbonation. The goal in both cases is the same; enhance the capture carrying capacity of the sorbent and reduce the amount of CO₂ in the flue gases. It was decided to test the dolomites in two different pre-calcination atmospheres, namely, 25% of CO₂/ 75% of N₂ and 100% N₂. In the case of using 25% in the pre-calcination, the process included two steps: first, 10 minutes calcination at 800 °C with 25% of CO₂ and 75% of N₂, then the second, only with 100% of N₂ at 800 °C until the end of calcination.

Two different conditions for CO₂ gas feed composition during the carbonation were chosen: 15% was used to reflect the amount of CO₂ in the flue gases which are usually released from coal power plants and 25% which is the amount of CO₂ which is released from cement production.

The table 5 shows the tests performed to evaluate the performance of the CO₂ carrying capacity of the selected dolomite.

Table 5 Summary of the tests performed to evaluate the CO₂ carrying capacity of the selected dolomite β

Pre-calcination atmosphere	Carbonation atmosphere	Number of calcination carbonation cycles
100% N ₂	15% CO ₂ (85 % N ₂)	0
		10
		20
	25% CO ₂ (75 % N ₂)	0
		10
		20
25% CO ₂ +75% N ₂	15% CO ₂ (85% N ₂)	0
		10
		20
	25% CO ₂ (75% N ₂)	0
		10
		20

Additional test using MgO as a sorbent was carried out to understand the role of this oxide on CO₂ capture and carrying capacity.

4. Results and Discussion

This study allowed comparing the reactivity of the dolomites with other natural sorbents. First, the two previously mentioned dolomites were studied, then the dolomite sample with the best performance was selected to carry out complementary studies under different conditions in the fixed bed unit laboratory scale unit. The characterization of the used and fresh sorbent samples was performed by X-ray diffraction, SEM and N₂ sorption. The results will indicate future research directions that can be followed for the use of dolomites in the industrial CO₂ capture applications.

4.1 Comparison of two natural dolomites

Figure 2 presents the XRD patterns of both sorbents. Both dolomites exhibit the Ca_{0.5}Mg_{0.5}CO₃ peak and it is possible to confirm that some Ca is present as CaCO₃, however, MgCO₃ wasn't identify individually.

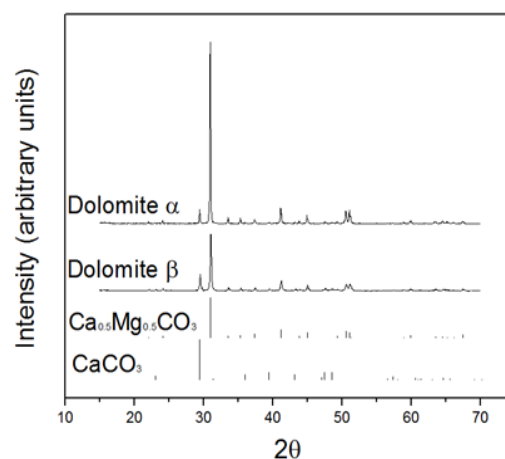


Figure 2 XRD patterns of dolomite α and dolomite β

Figure 3 shows the N₂ sorption isotherms of fresh dolomite α and β . The isotherms are type II which are typical for non-porous and macroporous sorbent. The S_{BET} of fresh dolomite β is higher (about 2 times) than dolomite α but the total pore volume is the same.

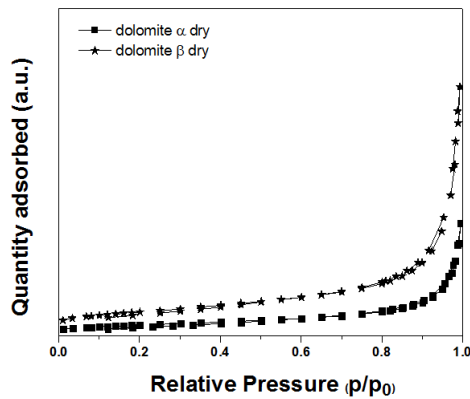


Figure 3 N₂ sorption isotherms of fresh dolomite α and β

Table 6 presents the specific surface area, S_{BET} and the total pore volume of both dolomites, V_p (not including microporous with mean pore width higher than 1000 Å).

Table 6 Specific surface area and total pore volume of dolomite α and β

Sorbents	S_{BET} (m ² /g)	V_p (cm ³ /g)
Dolomite α	2.35	0.006
Dolomite β	5.13	0.013

Figure 4 presents the morphological aspect of both dolomites when the sorbent samples were magnified in SEM 5000x.

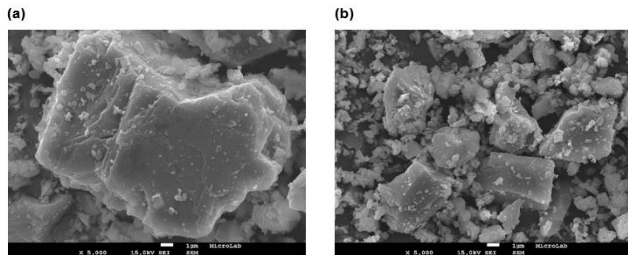


Figure 4 SEM images of dolomite α (a) and dolomite β (b)

Comparing SEM photos illustrated in Figure 4 of fresh dolomite α with dolomite β , dolomite α has less small particles than dolomite β . This is in the agreement with the data shown in table 2, which confirms that dolomite β sample has smaller particles.

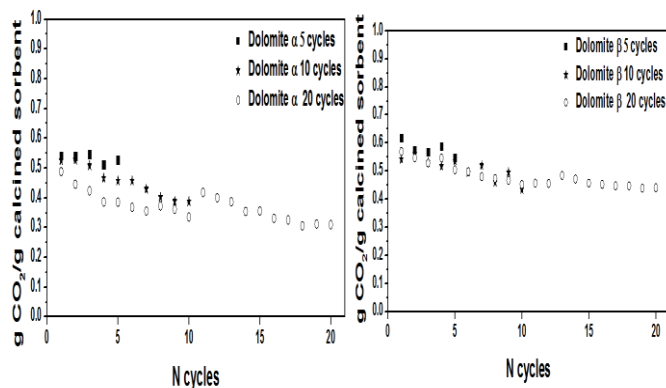


Figure 5 Comparison of CO₂ carrying capacity for dolomite α and β

It can be observed (Figure 5) that dolomite β has a higher initial CO₂ capture capacity (10% higher). Probably, it can be partly justified by the slightly increase of calcium content in dolomite β comparatively with dolomite α (Table 3) and to the different mean particle sizes of the two dolomites (2.5 μ m vs. 6 μ m, Table 2).

The theoretical maximum carrying capacity for dolomite α is 0.875 gCO₂/g(CaO+MgO) in dolomite α calcined and for dolomite β is equal to 0.864 gCO₂/g(CaO+MgO).

The estimation was based on the theoretical CO₂ carrying capacity of CaO and MgO, respectively, 0.78 g CO₂/g CaO and 1.09 g CO₂/g MgO and attending to the chemical composition of dolomites (Table 3).

Theoretically, comparatively with dolomite β the carrying capacity of dolomite α should be slightly higher because of the higher MgO content. However, the MgO present should be almost inert, which means that only CaO should react along the carbonation-calcination cycles and lower carrying capacities are observed.

Textural properties were evaluated by N₂ sorption for dolomite α and dolomite β . Figure 6 compares the N₂ sorption isotherms, which are obtained for the different number of cycles (0, 5, 10 and 20 cycles). All the isotherms are type IV and present a hysteresis that is typical for mesoporous solid material.

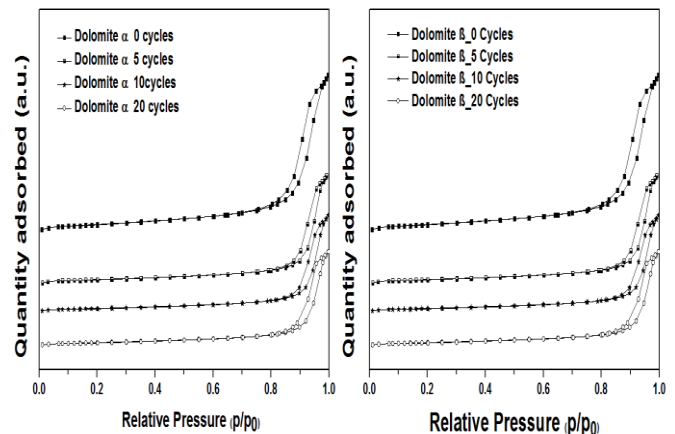


Figure 6 N₂ sorption isotherms for the used dolomite α and dolomite β samples along the cycles

Table 7 presents S_{BET} and V_p for both dolomites tested in the fixed bed reactor for the different number of cycles. The data provides insight into the carrying capacity differences between the two types of dolomites. In both cases, S_{BET} and V_p decrease along the cycles. Dolomite β , which has better carrying capacity, has higher S_{BET} in the end of the 20 cycles. These results could explain the improvement of CO₂ capture of dolomite β . Dolomite α has smaller S_{BET} and lower ability to capture CO₂ compared to dolomite β , which has higher S_{BET} .

It is known that sintering is one of the main reasons for the loss of sorbent reactivity, which is justified by the decrease of S_{BET} along the cycles. All the observations are in agreement with the results found in the literature [17].

Table 7 BET specific surface area and total pore volume for dolomite α and β

Sorbents	Number of cycles	S_{BET} (m ² /g)	V_p (cm ³ /g)
Dolomite α	0	51	0.29
	5	27	0.17
	10	21	0.11
	20	19	0.11
Dolomite β	0	47	0.26
	5	28	0.16
	10	23	0.14
	20	23	0.13

Figure 7 presents the correlation between S_{BET} for the used samples and CO_2 capture deactivation (difference between the first and n^{th} cycle carrying capacity) for $n=5, 10$ and 20 . For each dolomite, the carrying capacity observed in the 1st cycle was considered as reference value. Figure 7 shows a direct inverse proportional relation between S_{BET} and the deactivation of the sorbent, i.e., when the S_{BET} decreases the deactivation of sorbent increases. For 20 cycles, the deactivation was 36% and 23% for dolomite α and dolomite β , respectively. These results also indicate that for the same S_{BET} , dolomite β has a lower CO_2 capture deactivation, meaning that the decrease of S_{BET} along the cycles is not the only reason for the sorbents deactivation. This is also in agreement with the results presented by Pinheiro and *et al.* [18] for waste marble powder sorbents.

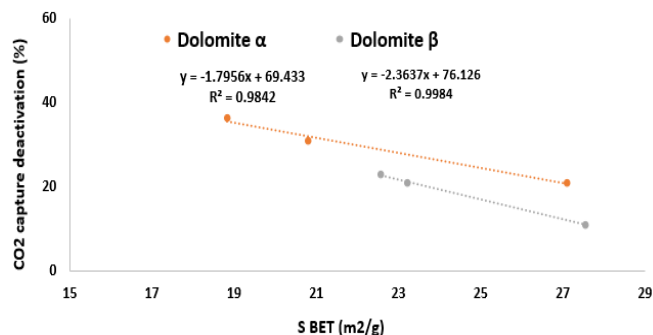


Figure 7 Relation between CO_2 capture deactivation (%) and the specific surface area

It can be observed that CaO and MgO crystallite size increase along the number of cycles (Figure 8). These changes can be related to the sintering of the sorbent, which occurs in the calcination/carbonation reactions in the fixed bed reactor. When compared to the dolomite β , in the case of dolomite α the CaO crystallite size is higher and after 20 cycles is around 49 nm. For dolomite β , after 20 cycles the CaO mean crystallite size is around 44 nm. In case of MgO, after 20 cycles the crystallite size is 28 nm and 24 nm for dolomite α and dolomite β , respectively. Zhu *et al.* [19] with the implementation of Scherrer's equation, found similar results for dolomites respectively, 38 nm and 22 nm for CaO and MgO.

Wang *et al.* [16] evaluated the crystallite size when different experimental conditions were implemented and verified that it could change between 45-93 nm for CaO and 33-69 nm for MgO. The higher values were observed for calcinations performed at 950 °C.

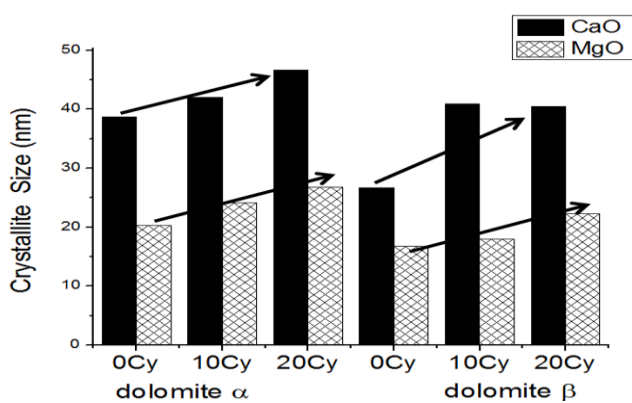


Figure 8 Crystallite Size for dolomite α and dolomite β along the cycles

SEM images of dolomite α and dolomite β were magnified 70000x, after 20 cycles are illustrated in Figure 9. In both cases, it can be observed the presence of small grains (solid line circle) and more dense and compacted regions (dash circle). Due the limitations of SEM technique it is difficult to accurately identify a Ca and Mg presence in specific zones of the sorbent.

Only HR Transmission Electron Microscopy (TEM) technique allows to confirm accurately the CaO and MgO zones. Apparently, dolomite α presents more segregated and compacted particles, as it can be seen in dashed line circle and the dolomite β presents less segregation, less compaction and more voids between particles. This could justify the lower CO_2 carrying capacity of dolomite α , i.e., the diffusion of CO_2 molecule inside the pores is more difficult in dolomite α .

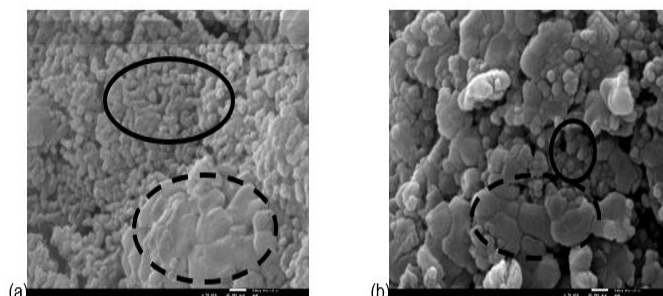


Figure 9 SEM images of the dolomite α (a) and dolomite β (b) after 20 cycles (70000x)

The comparison on both dolomites is shown in the Table 8. Based on the results included in the Table 8 dolomite β was selected due to its better performance for CO_2 capture, to be tested under different pre-treatments conditions. This study is important due to the strong need to improve the sorbents performance that could be economically, technically and environmentally viable.

Table 8 Comparison of dolomite α and dolomite β

Dolomite α	Dolomite β
Lower initial CO_2 capture	Higher initial CO_2 capture
Higher Loss of CO_2 capacity (after 20 Cycles)	Lower Loss of CO_2 capacity (after 20 Cycles)
Smaller S_{BET} (after 20 Cycles)	Higher S_{BET} (after 20 Cycles)
Lower V_p	Higher V_p
Higher CaO and MgO crystallite size	Lower CaO and MgO crystallite size

4.2 Influence of pre-calcination and carbonation atmosphere on CO_2 carrying capacity

This section presents the study of the influence of different pre-calcination conditions (100% of N_2 or 25% of CO_2) and different CO_2 gas feed composition (15% and 25%) during the carbonation step in dolomite β carrying capacity. There were performed tests with 10 and 20 cycles. For comparative reasons, it was performed a 0 cycles test, for the different pre-calcinations conditions.

The performance of dolomite was compared in terms of the CO_2 capture efficiency and it is presented in Figure 10 as a function of the number of cycles and for different pre-calcination atmospheres and CO_2 % in the carbonation step.

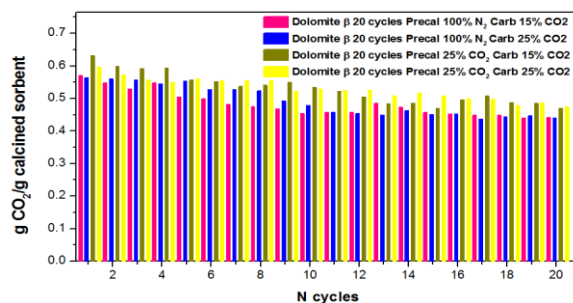


Figure 10 Influence of different pre-calcination and carbonation atmospheres in CO_2 carrying capacity of dolomite β for 20 cycles

The results showed that the initial carrying capacity is higher in the case of the dolomite pre-calcined with 25% of CO₂, which means that the pre-calcination atmosphere influences the carrying capacity. The influence of CO₂ % during the carbonation seems to be less relevant, especially when the number of cycles increase. The results confirmed that the use of 25% of CO₂ in the gas mixture during the carbonation step, did not influence significantly the dolomite performance as a sorbent. As it is known from the literature, dolomite decomposes in a two-step process in the presence of CO₂ in the reactor. This result in a higher and more stable uptake of CO₂ compared to the results from the pre-calcination only with N₂ [20] as it also can be observed in the results shown in Figure 10.

The XRD patterns of the sorbent samples half calcined were evaluated after the half pre-calcination step for both 100% of N₂ and 25% of CO₂ atmospheres, at 800 °C. In the first case, the sorbent was fed into the reactor and the temperature was increased until 800 °C, when this temperature was reached the calcination was stopped and the sample was collected.

In the second case, the sample was heated until 800 °C with a 25% CO₂ atmosphere, and remained at this temperature for 10 minutes before the calcination was stopped. Both samples were analyzed by XRD (Figure 11).

As can be observed in Figure 11 it is very difficult to distinguish between the CaCO₃ and Ca_{0.94}Mg_{0.06}(CO₃)₂ patterns. However, based on the database information (COD), it was accepted that during the half pre-calcination with 25% of CO₂ it was formed CaCO₃ and eventually some Ca_{0.94}Mg_{0.06}(CO₃)₂. In the case of half pre-calcination only with N₂, the presence of CaCO₃ appears to be less probable. MgO and CaO were identified in both XRD patterns.

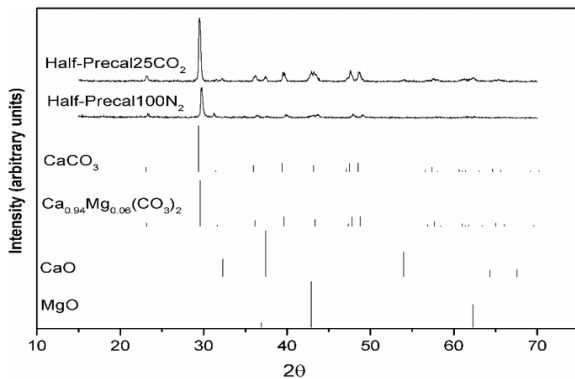


Figure 11 XRD patterns of dolomite β pre-calcined under different atmospheres

The carrying capacity of the tested dolomites for 10 and 20 cycles are shown in Figure 12. It can be observed a good repeatability and agreement between the tests performed in the same experimental conditions.

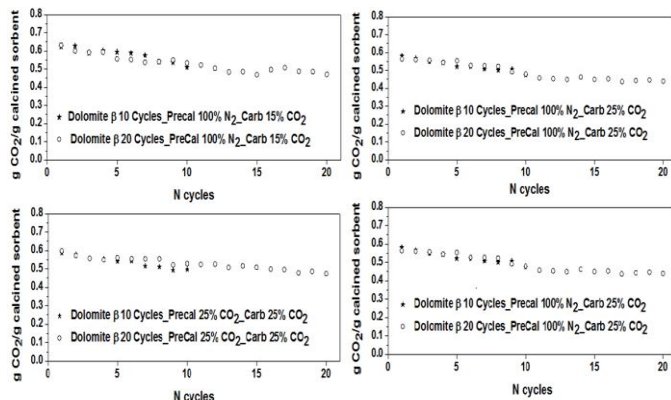


Figure 12 Carrying Capacity of dolomite β using different experimental conditions (10 and 20 cycle's tests)

The best results were selected from Figure 10 and compared with the results previously obtained within CaReCI project with other natural sorbents. From the analysis of Figure 13, one can conclude that:

- in the 1st cycle, the carrying capacity of CaCO₃ and WMP β are similar, but lower for dolomite β probably due the lower Ca amount in this last sorbent,
- after 5 cycles, comparatively with CaCO₃ and WMP, dolomite presents a higher CO₂ carrying capacity,
- the best results are obtained for dolomite β pre-calcined in 25% of CO₂ where it is observed an improvement of the carrying capacity along the cycles and a lower sorbent deactivation in the end of the 20 cycles, (Figure 10)
- the thermal pre-calcination atmosphere leads to the different sorbent performances (Figure 10)

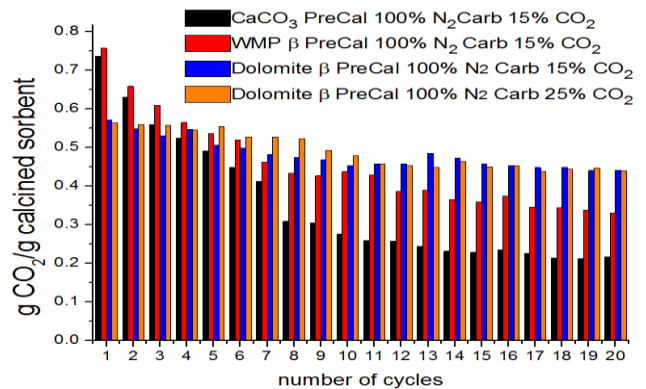


Figure 13 Carrying Capacity of CaCO₃, WMP (waste marble powder) and dolomite β pre-calcined with 100% of N₂

Figure 14 shows, that for all cases, there is an initial high decrease in S_{BET} and V_p between 0 and 10 cycles, but from 10 to 20 cycles those properties do not have significant changes. This result is in agreement with the dolomite CO₂ carrying capacity profiles along the 20 cycles previously presented in Figure 10. Concerning the effect of the pre-calcination atmosphere, it was observed that it influences the textural properties of the dolomite for 0 cycles. The S_{BET} was around 47-51 m²/g and 37-38 m²/g for 100% of N₂ and 25% of CO₂ pre-calcination atmospheres, respectively (Figure 14). Comparing these values, it can be concluded that pre-calcination under CO₂ reduces the initial surface area of the sorbent, however during the carbonation-calcination cycles the sorbent CO₂ carrying capacity is higher for the cases of pre-calcination with an atmosphere with CO₂ and a lower deactivation is observed (Figure 10). This means that the CO₂ carrying capacity does not only depend on the S_{BET} , and probably, the de-mixing of CaO and MgO during the CO₂ pre-calcination, contributes to a more stable sorbent structure/skeleton, and a strong stabilisation of the sorbent is observed from the first cycles. In the dolomites, due to the MgO presence, the pre-calcination with CO₂ contributes to a faster stabilization of the sorbents that show a lower difference in the textural properties between 0 and 10 cycles. That leads to the conclusion that thermal pre-treatment of dolomites affected the textural properties in the firsts cycles but after some cycles, it stabilizes and after 20 cycles the S_{BET} is of the same order for all the other pre-treatments cases.

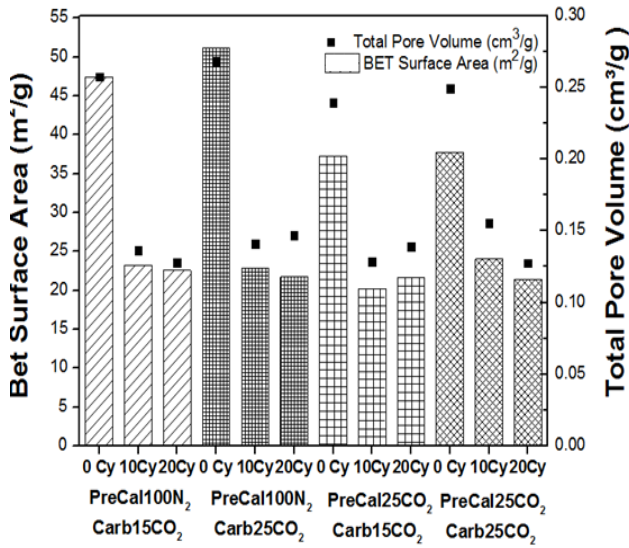


Figure 14 Comparison of S_{BET} and V_p of dolomites tested using different experimental condition

Pore size distribution evaluated by BJH method (desorption branch) is illustrated in Figure 15. The results show that for the sorbents pre-calcined with CO_2 the average pore width stabilized, i.e., for 0, 10 and 20 cycles the average pore width was stabilized around 300 Å and did not increase. For the case of pre-calcination only with N_2 , for 0 cycles the average pore width was around 200 Å, but for 10 and 20 cycles it increased to around 300 Å. This is in agreement with the data presented in Figure 15, where it was verified that the pre-calcination with CO_2 contributes to a faster stabilization of the sorbents textural properties, including the pore size distribution.

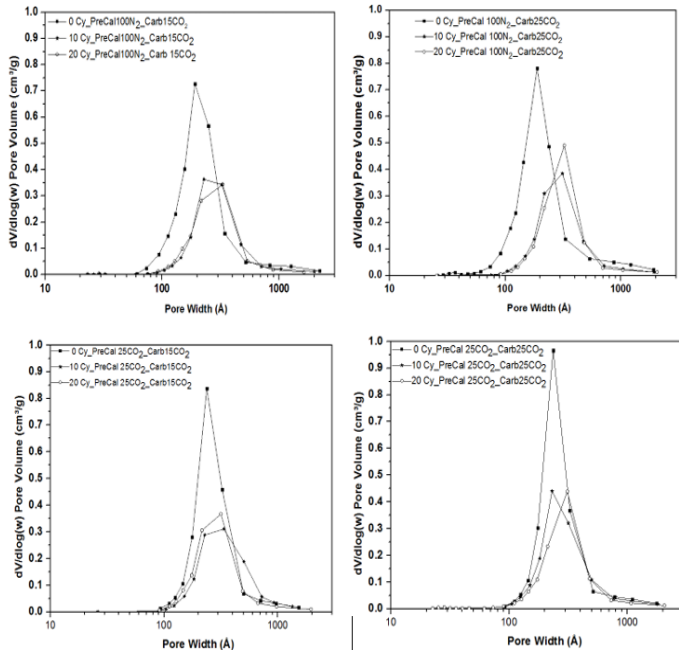


Figure 15 Pores size distribution (PSD from BJH desorption branch) for used dolomites

Figure 16 shows the results of XRD analysis for the four different conditions tested for the dolomite β . The presence of CaO and MgO was confirmed and no mixed phases were observed between CaO and MgO. It can be stated that in the end of the calcination steps, all the dolomite sorbents are mainly composed by CaO and MgO when they are ready for a new carbonation.

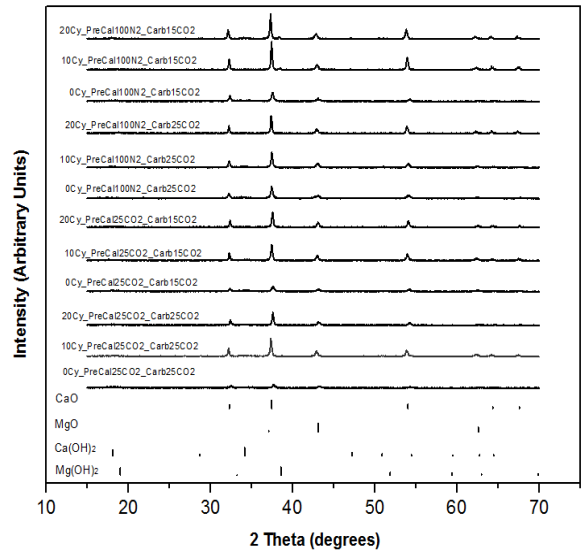


Figure 16 Comparison of X-ray patterns of dolomite β tested under different experimental conditions

The relevant information from Figure 17 is related with the higher CaO crystallite size of sorbents pre-calcined with 100% of N_2 , comparatively with the pre-calcined with 25% of CO_2 . This was especially evident when 0 cycles experiments were compared. These results confirm that the pre-calcination with 25% of CO_2 delays the CaO sintering, especially in the first calcination-carbonation cycles. Wang *et al.* [16] performed 30 calcination-carbonation cycles using different pre-calcination atmospheres and observed a CaO crystallite size of 54 nm and 45 nm for a dolomite pre-calcined with 100% N_2 and 100% CO_2 , respectively. These authors stated that “the presence of the Mg-calcite phase hindered the demixing of Ca and Mg, which delayed the sintering of CaO particles over repeated carbonation/calcination cycles” [16]. After 20 cycles, the difference between the crystallite sizes are smaller which evidence that the pre-calcination atmosphere loses relevance.

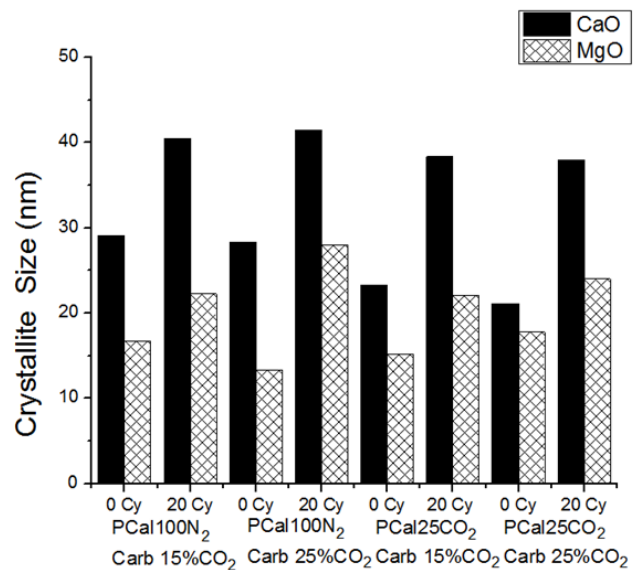


Figure 17 Crystallite Grain Size for different pre-calcination of dolomite

The carbonation adsorption profile in the first cycle (15% of CO₂) for dolomite β under different pre-calcination atmospheres was compared with those obtained for CaCO₃ and MgO (Figure 18). Two carbonation stages can be observed; the first fast carbonation that is chemically controlled and a second slow carbonation stage that is controlled by the diffusion of the CO₂ in the sorbent.

In the case of MgO, no carbonation was observed at 700°C. Reactivity tests were performed with MgO samples using different carbonation/calcination temperatures: 700 °C/800 °C, 600 °C/700 °C, 500 °C/600 °C and 300 °C/400 °C. The results showed that MgO didn't capture CO₂ along the cycles. The main reason for the lack of CO₂ capture capacity by MgO, are the interactions between Mg²⁺ and O²⁻, which are very strong and disenable to destroy the bonds. Moreover, similar studies confirmed that pure MgO has low CO₂ capture capacity which is the reason of slow kinetic reactivity [20]. Comparatively with the CaCO₃ sorbent, dolomites show a lower deactivation with the increasing number of cycles, which could be related to the lower CO₂ diffusion limitations in this sorbent. Due to the presence of MgO particles, the CaO are not so close to each other so, the blockage due to the formation of the CaCO₃ layer during the carbonation is less relevant and the CO₂ diffusion along the dolomite is easier, which means that less time is needed in the carbonation step. In Figure 18, as expected it can be observed, that the diffusion stage of the first cycle carbonation is slower for the case of the CaCO₃ sorbent.

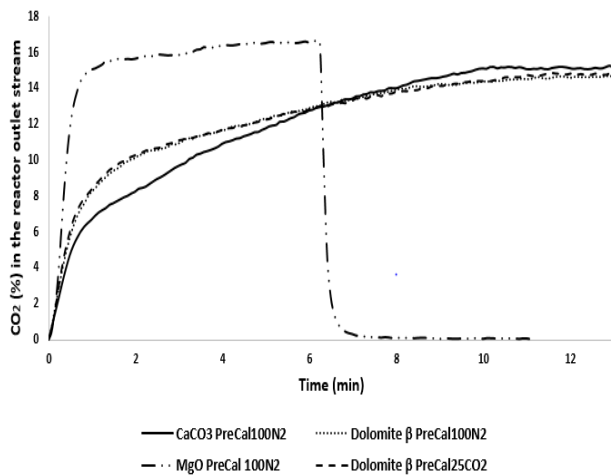


Figure 18 Comparison of carbonation profile of different sorbents

All the used sorbents were analysed by SEM after 20 cycles and the images are presented in Figure 19. The aim was to find the relationship between the morphological aspect and the sorbents carrying capacity. The magnification (40000x) was the same for all the samples. It was possible to distinguish two types of morphologies: zones with small particles, especially for samples pre-calcined and carbonated with 25% of CO₂ (Figure 19(d)) and zones more compacted, apparently sintered. Martos *et al.* [21] found the same type of morphology for dolomite after 20 cycles and identified the smaller particles as MgO and the zones more compacted as sintered CaO. The appearance of sintered zones was more visible for sorbents pre-calcined with 100% of N₂, as indicated by the dark circles, especially when compared with image (19 d). As the presence of CaO sintered particles are related with the sorbents deactivation, this agrees with the lower carrying capacity of sorbents pre-calcined with 100% of N₂.

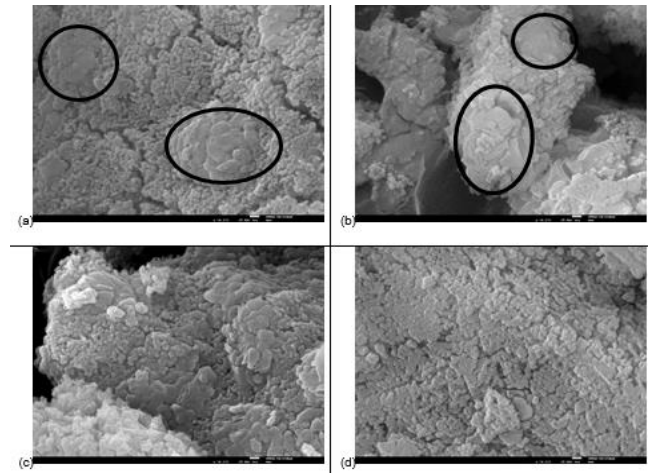


Figure 19 SEM images of dolomite β (a) Pre-cal: 100% N₂, Carb: 15%; (b) Pre-cal: 100% N₂, Carb: 25% CO₂; (c) Pre-cal: 25% CO₂, Carb: 15% CO₂; (d) Pre-cal: 25% CO₂ with Carb 25% CO₂ (magnification 40000x)

The results show that the best sorbent performance was obtained in the case of dolomite pre-calcined with 25% of CO₂ tested with 15% of CO₂ in the gas mixture in the carbonation steps, so these conditions were used in an experiment with 50 cycles of carbonation/calcination (Figure 20).

The 50 carbonation/calcination cycles were performed in the fixed bed reactor for 5 days, where the oven was turned off and a lower constant flow of nitrogen was maintained during the night. All the parameters like temperature and time of calcination and carbonation were controlled manually. The first 20 cycles have a decreasing linear carrying capacity. A deviation in the uptake can be noticed before completion of the 30th cycle. It was caused by the problem with accidentally lack of N₂ in the laboratory in the night and that is the reason why N₂ flow was not stabilised. After the 50 cycles, the dolomite β still has a carrying capacity of 0.34 g CO₂/g sorbent. The CO₂ carrying capacity data of Figure 20 was compared with data from Figure 13. The comparison shows that after 20 cycles the CaCO₃ and WMP carrying capacity is around 0.22 and 0.33 g CO₂/g sorbent, which means that the dolomite β pre-calcined with 25% of CO₂, even after 50 cycles still presents a better capture performance than CaCO₃ and is similar to WMP for 20 cycles.

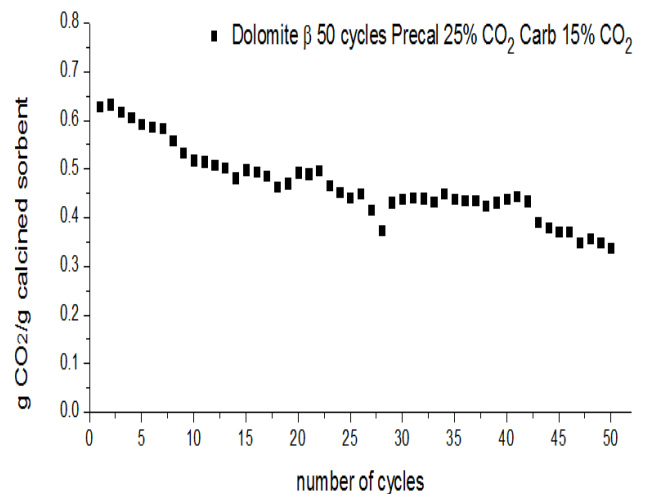


Figure 20 Carrying Capacity of the dolomite β through 50 cycles

Figure 21 presents the carbonation profiles for the different number of cycles of the 50 cycles experiment, namely: 1, 10, 20, 30, 40 and 50 cycles. The time for reaching complete carbonation decreases along the increasing number of cycles, and the slope of the first fast chemically controlled carbonation step increases with the number of cycles. This result is in agreement with the results presented in Figure 7, and can be explained by a decrease of the number of sorbent CaO molecules available at the beginning of each carbonation step for the reaction with CO₂ due to the increase of sorbent sintering and pore blockage with the number of cycles.

In the beginning of the cycle 1, the role of CO₂ diffusion between the CaO and MgO grains is more relevant, in spite of the CaCO₃ layer formed along the CaO and the lower pore size of sorbent there is some degree of diffusion. With the increase of number of cycles, the CaO and MgO crystallite size increases and can occur pores blockage (lower specific surface area), which hinders the CO₂ diffusion along the sorbent. The CaCO₃ layer formed during the carbonation step emphasizes this.

The diffusion is one of the main factors which influences the decreasing of the carrying capacity because of the formation of the carbonate layer.

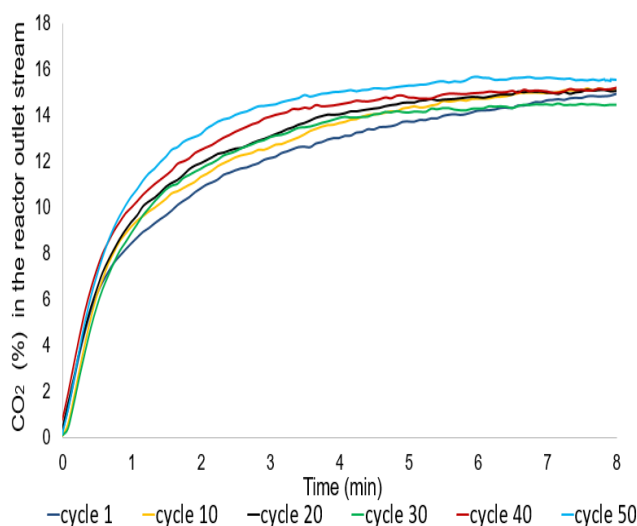


Figure 21 Graphical representation of carbonation conversion of dolomite β during 50 cycles presented for chosen cycle-number

5. Conclusions

The Carbon Capture and Storage Technologies are important solutions to prevent climate changes. Considering the aim to reduce GHG emissions with main focus on CO₂, the high-temperature Ca-looping for CO₂ capture is a promising technology to decrease the level of greenhouse gases emission in the atmosphere. The CO₂ uptake performance of two natural dolomite samples (α and β) as Ca-looping regenerable sorbents were investigated in this work under different conditions with the aim of improving the CO₂ capture capacity and overcoming the problem of sintering and pore blockage deactivation along the carbonation/calcination cycles which can limit the application of natural sorbent.

It was observed that the naturally occurring dolomite sorbents studied can be used as solid sorbents for CaL CO₂ capture with a high carrying capacity and stability along the cycles. As for other natural sorbents, the decrease in the carrying capacity along the cycles is also observed for both dolomites and can be directly related with the decrease of the specific surface area and increase of CaO and MgO crystallite size. But the results indicate that for the same S_{BET} , dolomite β has a lower CO₂ capture deactivation, meaning that the decrease of S_{BET} along the cycles is not the only reason for the sorbents deactivation. This is also in agreement with the results presented by Pinheiro *et al.* [18] for WMP sorbents.

The best carrying capacity was obtained for dolomite β , pre-calcined with 25 % of CO₂. It was concluded that pre-calcination of dolomites with CO₂, not only under pure N₂ resulted in a higher and more stable carrying capacity. Probably, the de-mixing of CaO and MgO during the CO₂ pre-calcination, contributes to a more stable sorbent structure/skeleton, and a strong stabilization of the sorbent is observed from the first cycles. Besides, this result shows that the S_{BET} is not the only reason for the sorbents deactivation.

Another test carried out with the 50 cycles of the dolomite pre-calcined with 25% of CO₂ and with 15% of CO₂ during the carbonation showed that after 50 cycles the dolomite sorbent presents a better CO₂ capture performance than CaCO₃ and is similar to the carrying capture capacity of the waste marble powder for 20 cycles.

The analysis of the different carbonation profiles obtained for the 50 cycles experiment revealed that the time for reaching complete carbonation decreases along the increasing number of cycles, and the slope of the first fast chemically controlled carbonation step increases with the number of cycles. Therefore, it can be concluded that there is a decrease of the number of sorbent CaO molecules available at the beginning of each carbonation step for the reaction with CO₂ due to the increase of sorbent sintering and pore blockage with the number of cycles.

In the first cycles, the role of CO₂ diffusion between the CaO and MgO grains is more relevant, in spite of the CaCO₃ layer formed along the CaO and the lower pore size of sorbent there is some degree of diffusion. With the increase of number of cycles, the CaO and MgO crystallite size increases and can occur pores blockage (lower specific surface area), which hinders the CO₂ diffusion along the sorbent. The CaCO₃ layer formed during the carbonation step emphasizes this.

The results obtained in this work are promising and confirmed that dolomites have high CO₂ carrying capacity and stability, that can be improved so that dolomites can be used in power plants or other industries where flue gases CO₂ concentration is around 10-15% and in cement industry, where the CO₂ concentration is around 25-30%.

6. References

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