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**Blending wastes of marble powder and dolomite sorbents for Calcium-Looping CO<sub>2</sub> capture under realistic calcination conditions**  
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<b>Abstract:</b>	The use of cheap and abundant natural materials based on wastes of marble powder (WMP) and dolomite as sorbents for CO <sub>2</sub> capture is extremely appealing to make Ca-looping (CaL) technology a more sustainable and eco-friendly process. Furthermore, for the downstream utilization of CO <sub>2</sub> it is more convenient that the calcination step during CaL process occurs under a concentrated CO <sub>2</sub> atmosphere, which implies higher calcination temperatures (>900°C), however these conditions are rarely used in experimental research tests, especially using natural sorbents and laboratory scale reactors. To fill this gap, in the present work the experimental CaL tests were carried out in a fixed bed reactor under mild (800°C, N <sub>2</sub> ) and more realistic (930°C, 80%CO <sub>2</sub> ) calcination conditions and the results were compared. A blend of WMP with dolomite was also tested as an approach to improve the stability and the CO <sub>2</sub> carrying capacity of WMP, since the MgO from dolomite should provide a barrier effect hindering the CaO sintering. Promising results are found when using a blended sorbent of WPM with dolomite. As regards the more realistic calcination under high CO <sub>2</sub> concentration at high temperature, there is a strong synergistic effect of inert MgO grains of calcined dolomite in the blended WMP+dolomite sorbent that leads to an improved stability along the cycles when compared with both WMP and dolomite used separately as sorbents. Blending WMP with dolomite is found as a promising approach to tailor cheap wastes-based blended sorbents with improved carrying capacity and stability along the cycles under realistic calcination conditions.
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To Professor Sang-Eon Park  
Editor-in-Chief of  
Journal of CO<sub>2</sub> Utilization

Lisbon, September 28, 2020

Dear Editor,

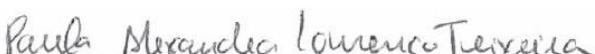
We are submitting online our paper entitled "**Blending wastes of marble powder and dolomite sorbents for Calcium-Looping CO<sub>2</sub> capture under realistic calcination conditions**", Paula Teixeira, Auguste Fernandes, Filipa Ribeiro, Carla I.C. Pinheiro, for publication in the international Journal of CO<sub>2</sub> Utilization.

The innovative results presented in a previous study (Pinheiro *et al.*, 2016) by these authors, show that natural Portuguese waste marble powders (WMP) have potential to be an economically attractive option to be used as cheap CaO-based sorbents for CO<sub>2</sub> post combustion capture. Nevertheless, for the downstream utilization of CO<sub>2</sub> it is more convenient that the calcination step during Ca-Looping process occurs under a concentrated CO<sub>2</sub> atmosphere, which implies higher calcination temperatures (> 900 °C), however these conditions are rarely used in experimental research tests, especially using natural sorbents and laboratory scale reactors. The present work intends to fill this gap, and the experimental CaL tests were carried out in a fixed bed reactor under mild (800 °C, N<sub>2</sub>) and more realistic (930 °C, 80% CO<sub>2</sub>) calcination conditions and the results were compared.

A blend of WMP with natural dolomite was also tested as an approach to improve the stability and the CO<sub>2</sub> carrying capacity of WMP. The authors found that it is a promising approach to tailor cheap wastes-based blended sorbents with improved carrying capacity and stability along the cycles under realistic calcination conditions, and should be encouraged as a bi-ecofriendly material for the CaL process due to the advantages of contributing to reduce the cost of the cyclic CaL CO<sub>2</sub> capture process, as well as to minimizing the adverse environmental impacts of the high volume of WMP generated.

Hoping to hear from you soon, with my best regards

Dr. Paula Teixeira

  
(Corresponding author)

# Blending wastes of marble powder and dolomite sorbents for Calcium-Looping CO<sub>2</sub> capture under realistic calcination conditions

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## ABSTRACT

The use of cheap and abundant natural materials based on wastes of marble powder (WMP) and dolomite as sorbents for CO<sub>2</sub> capture is extremely appealing to make Ca-looping (CaL) technology a more sustainable and eco-friendly process. Furthermore, for the downstream utilization of CO<sub>2</sub> it is more convenient that the calcination step during CaL process occurs under a concentrated CO<sub>2</sub> atmosphere, which implies higher calcination temperatures (>900°C), however these conditions are rarely used in experimental research tests, especially using natural sorbents and laboratory scale reactors. To fill this gap, in the present work the experimental CaL tests were carried out in a fixed bed reactor under mild (800°C, N<sub>2</sub>) and more realistic (930°C, 80%CO<sub>2</sub>) calcination conditions and the results were compared. A blend of WMP with dolomite was also tested as an approach to improve the stability and the CO<sub>2</sub> carrying capacity of WMP, since the MgO from dolomite should provide a barrier effect hindering the CaO sintering. Promising results are found when using a blended sorbent of WPM with dolomite. As regards the more realistic calcination under high CO<sub>2</sub> concentration at high temperature, there is a strong synergistic effect of inert MgO grains of calcined dolomite in the blended WMP+dolomite sorbent that leads to an improved stability along the cycles when compared with both WMP and dolomite used separately as sorbents. Blending WMP with dolomite is found as a promising approach to tailor cheap wastes-based blended sorbents with improved carrying capacity and stability along the cycles under realistic calcination conditions.

**Keywords:** CO<sub>2</sub> capture; Ca-looping; sorbents; waste marble powder; dolomite

## **1. INTRODUCTION**

Paris Agreement signed in 2016 has as main target “to hold the increase of the global average temperature well below 2 °C above pre-industrial levels and to pursue efforts to limit the temperature increase to 1.5 °C above pre-industrial levels”[1]. The Global CCS Institute report concluded that the extra costs of CO<sub>2</sub> capture and the absence of policies to justify investment are primary barriers to large-scale deployment of carbon capture and storage (CCS) in power generation, but a good progress has been made to reduce the cost and to optimize the carbon capture technologies performance. Additionally, CCS is considered a key option available for deeply decarbonizing cement, steel and iron production [2].

Ca-looping (CaL) is one of the most promising second-generation technologies for the cement industry post-combustion CO<sub>2</sub> capture, based on the reversible chemical reaction of CaO and CO<sub>2</sub> to form CaCO<sub>3</sub>, but it still has some limitations related with the sintering of CaO sorbents and consequently with the decrease of the sorbents CO<sub>2</sub> capture capacity during the cyclic operation. The selection of sorbents with high carrying capacity and stability is essential for the CaL technology implementation in large scale [3]. Comparatively with other technologies, in the CaL the sorbent can be easily regenerated and, additionally, the initial CO<sub>2</sub> capture efficiency is especially high during the initial carbonation - calcination cycles. During the calcination step, the CO<sub>2</sub> can be selectively separated from CaCO<sub>3</sub>, and if this step is carried out under a high CO<sub>2</sub> partial pressure, a pure stream of CO<sub>2</sub>, suitable for storage or for conversion processes, can be generated. Furthermore, the CaL concept has unique potential advantages, i.e., it can be integrated in a variety of plants, and the exhausted sorbent (CaO) can be used as raw material in the cement plants, which allows the reduction of the carbon footprint of this industry that is responsible for 5 % of anthropogenic global CO<sub>2</sub> emissions [4-6]. Other advantage of CaL is the use of natural and non-expensive CaO-based sorbents, as limestone, which is a resource widely distributed and available on the Earth’s surface.

Natural limestone (CaCO<sub>3</sub>) is the perfect candidate for CO<sub>2</sub> capture, but its deactivation along the cycles under calcination temperatures higher than 800 °C, is significant and CaO conversion usually reaches very low values in the range 20-30 % after a few number of cycles [7]. Several efforts have been done to understand the mechanisms associated with the CaO based sorbents deactivation to increase their lifetime [8-9]. This loss of capacity is mainly attributed to the sorbents sintering and pore blocking. The sorbent sintering is correlated with the loss of micropores and mesopores and crystallite size growing along the cycles, causing the surface area and total pores volume reduction, and also changes in the pores

size distribution [10-13]. Some authors believe that the average pore size overrides the contribution of surface area [14]. In fact, dynamic simulations evidence that particles with higher separation distance have a larger CO<sub>2</sub> uptake due to a lesser occurrence of sintering [15]. Strategies for lifetime enhancement of CaO-based sorbents include: (1) surface modification using solid supports like inert porous alumina; (2) use of additives or dopants to obtain CaO-based mixed oxides with higher stability; (3) changing the morphology and microstructure, e.g. preparation of nano-particles; (4) use of different synthetic precursors with a rich microporous structure [7-8, 10,16-22].

Besides the advantages of synthetic and modified sorbents, at industrial level their use is limited by the associated energy costs. A compromise should be taken between the sorbent performance, cost and environmental issues, so practical, scalable and inexpensive CaO-based sorbents should be used [23]. To promote the industrial CaL process development and to move on to the next technology readiness level (TRL) step, it is necessary to guarantee the sustainability of this technology focusing on economic and ecological materials, i.e. by using an ecofriendly approach.

Due to environmental issues, solid sorbents recovered from waste resources [24-26], like waste marble powder (WMP), different kinds of biomass wastes, carbide slag and paper and pulp industry sludge, have been recently considered. Preliminary studies indicate that, among the wastes already proposed for CO<sub>2</sub> capture, the WMP composed mainly by CaCO<sub>3</sub> and vestigial amounts of other elements (Mg, Si, Al, Fe...), is one of the materials that presents very good performance for CO<sub>2</sub> capture, even when compared with the limestone.

The second natural carbonate most abundant in Earth's surface is dolomite, that contains calcium and magnesium in different proportions, Ca<sub>(1-x)</sub>Mg<sub>x</sub>(CO<sub>3</sub>)<sub>2</sub>. This mineral has been recently identified as an adequate precursor for CO<sub>2</sub> capture, but the role of MgO in CO<sub>2</sub> capture is not completely understood [27]. Thermodynamic data indicate that for temperatures between 600 and 700 °C and CO<sub>2</sub> partial pressures in the range 0.15 to 0.30 bar used during the carbonation step of Ca-looping process, MgO is almost inert [28-29], but previous studies evidenced higher CO<sub>2</sub> carrying capacity and stability for dolomite than for limestone [27]. The presence of chemical elements like Mg, Al and Si, during the carbonation-calcination cycles, influences the skeleton/microstructure of the calcined sorbent, which contributes to hinder aggregation or sintering of CaO crystallites and helps in preserving the nanocrystalline CaO structure [30]. However, more detailed studies are still necessary to understand the role of these elements and of MgO on the enhancement of the stability and multicycle carrying capacity performance observed for these alternative natural CaO-based sorbents, especially under a more realistic industrial calcination gas atmosphere with a high concentration of CO<sub>2</sub>.

With the purpose of a subsequent storage or utilization of captured CO<sub>2</sub>, the sorbents' calcination step should be conducted under more realistic and convenient gas atmospheres with a high concentration of CO<sub>2</sub>, which implies the use of calcination temperatures higher than 900 °C due to the reaction thermodynamic equilibrium. The use of concentrated CO<sub>2</sub> atmospheres approximating more realistic industrial CaL calcination conditions for generating an exit gas stream with a high concentration of CO<sub>2</sub> is still a challenge and is rarely found in the literature reporting experimental research tests performed at laboratory scale reactors [3], especially with natural sorbents. This work has the main goal of filling this gap for testing and comparing the performance of natural CaO-based sorbents such as WMP, dolomite and their blending, for cyclic CaL CO<sub>2</sub> capture using a calcination atmosphere with a realistic high concentration of CO<sub>2</sub>. The CaL tests were carried out in a fixed bed reactor using two different calcination conditions: (a) at 800 °C under 100% N<sub>2</sub> atmosphere, that will be called as "mild" calcination conditions in this work; and (b) at 930 °C under a gas atmosphere of 80% CO<sub>2</sub> balanced in N<sub>2</sub>, that will be called as "more realistic" calcination conditions in this work. A blend of WMP with dolomite was also tested as an approach to improve the sorbents carrying capacity.

## 2. EXPERIMENTAL SECTION

Samples of WMP and dolomite were used as CaO sorbent precursors. The WMP sorbent was collected in a Portuguese marble producer plant in the region of Estremoz (Portugal) and the dolomite sample (Omyadol SF-GZ) is from Turkey. A sample of blended sorbent with WMP and dolomite was prepared by mechanical mixture. It was prepared based on the CaO and MgO composition (wt. %) of the natural materials to obtain a sample with 80% of CaO and 20% of MgO in a calcined basis (wt. %). The samples were dried and kept at 120 °C before the experimental tests to eliminate the moisture. The elemental composition of WMP and dolomite was determined at LAIST (Laboratory of Analysis of Instituto Superior Técnico). Calcium, magnesium, aluminium, silicon and iron were analysed by inductively coupled plasma – optical emission spectrometry, and the carbon was determined by an internal method (accredited by Portuguese Institute of Accreditation). The elemental composition is essential to estimate the CO<sub>2</sub> capture capacity of the CaO sorbents along the carbonation-calcination cycles.

The BET specific surface area (S<sub>BET</sub>) and the pores size distribution (PSD) of the used sorbents after n cycles (n=0, 2, 5, 10, 20 cycles) of calcination-carbonation were assessed by N<sub>2</sub> sorption at -196 °C, on a Micromeritics ASAP 2010 apparatus. Before the analysis, the samples were outgassed under vacuum at 90 °C for 1 h and then at 350 °C for 5 h. The total pore volume (V<sub>p</sub>) was calculated from the adsorbed

volume of nitrogen for a relative pressure ( $P/P_0$ ) of 0.97. The BET equation was applied to estimate the  $S_{BET}$  and the PSD distribution was achieved by using BJH model (desorption branch).

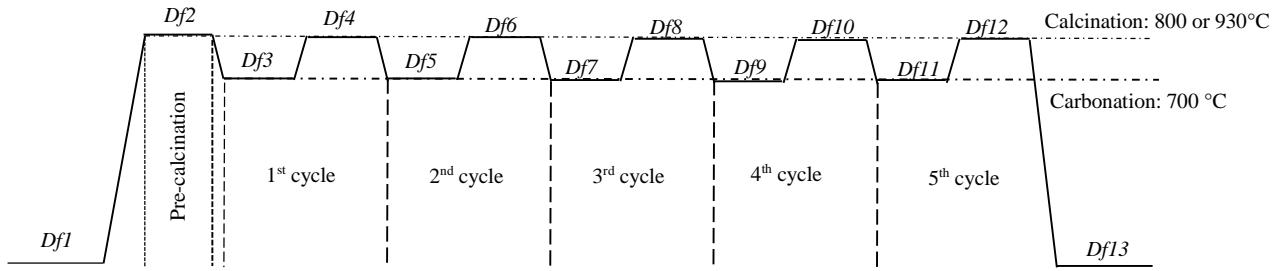
The macropores size distribution of the selected sorbents was determined by Hg porosimetry, using a Micromeritics Autopore IV 9500. During the test the pressure range varied between 0.5 and 30000 psi and a contact angle of 130 ° was considered.

In order to identify the different crystalline phases, powder X-ray diffraction (PXRD) diffractograms of fresh and used sorbents were obtained using a Bruker D8 Advance X-Ray diffractometer using Cu K $\alpha$  ( $\lambda = 0.15406$  nm) radiation operating at 40 kV and 40 mA. The measurements were made between 15-70 ° in 2 $\theta$ , with a step size of 0.03 ° and step time of 3 s. The crystallography open database (COD) was used to identify the crystalline phases and the TOPAS 4.2 software (Bruker) was used to quantify the amount of the different phases by means of Rietveld refinement. The crystallite size of sorbents was estimated using Scherrer's equation ( $D = K\lambda/b \cos \theta$ ), based on the XRD data. D is the crystallite size (nm), b is full width at half maximum (FWHM) of the XRD peak considered,  $\lambda$  is the wavelength (0.15406 nm),  $\theta$  is the Bragg angle (degree) and K is Scherrer's constant (K = 0.9, assuming that the particles are spherical).

## 2.1. Carbonation-calcination tests at *in situ* XRD chamber

*In situ* XRD carbonation – calcination cycles were carried out in a Bruker D8 Advance X-Ray diffractometer equipped with an Anton Paar HTK 16N High Temperature Chamber. The carbonation was performed at 700 °C and calcination at 800 °C or 930 °C, for mild or more realistic calcination conditions, respectively. To study the evolution of CaCO<sub>3</sub> and CaO crystalline phases along the carbonation-calcination cycles, the measurements were made between 28 and 39 ° in 2 $\theta$  for WMP, dolomite, and for the blended sorbent. The CaCO<sub>3</sub> peaks (29.3 ° and 35.9 °) and CaO peaks (32.3 ° and 37.5 °) profiles were evaluated. A step size of 0.05 ° and a step time of 1 s was used for all samples. A first diffractogram ( $DfI$ ) was carried out at room temperature and after each carbonation or calcination gas-solid reaction at high temperature. The carbonation or calcination reactions were carried out for 10 min and after this time the XRD diffractograms ( $Dfn$ ) were obtained. Fig. 1 shows the scheme of the procedure used. A flow of 100 ml was used along the carbonation-calcination cycles, 15% of CO<sub>2</sub> balanced in N<sub>2</sub> during the carbonation, and 100% of N<sub>2</sub> or 80 % of CO<sub>2</sub> balanced in N<sub>2</sub> for mild and more realistic calcination conditions, respectively. The heating temperature rate between 700 and

800/930 °C was 20 °C/min while the cooling temperature rate between 800/930 °C and 700 °C was 50 °C/min.



**Fig. 1.** *In-situ* XRD carbonation-calcination cycles procedure

The recorded XRD diffractograms were analyzed using TOPAS 4.2 software (Bruker) and the relative amounts of CaCO<sub>3</sub> and CaO, based on the patterns obtained in the range 28-39 ° in 2θ, were quantified by means of Rietveld refinement.

## 2.2. Carbonation-calcination tests in a fixed bed reactor

The cyclic carbonation and calcination reactions were carried out in an experimental laboratory-scale fixed-bed reactor system under mild (800 °C and 100% N<sub>2</sub>) and more realistic (930 °C and 80% of CO<sub>2</sub> flow balanced in N<sub>2</sub>) calcination conditions. The experimental system consists of a gas feeding system, a reactor system with temperature control, and a CO<sub>2</sub> gas analyser. The unit includes an oven and a quartz reactor with an internal diameter of 3 cm and a length of 10 cm and a porous plate to support the adsorbent. A stream of CO<sub>2</sub> and N<sub>2</sub> (for carbonation and more realistic calcination conditions) or only N<sub>2</sub> (for mild calcination conditions) was fed to the quartz reactor and the flows were controlled with Alicat and Brooks mass flowmeters, for N<sub>2</sub> and CO<sub>2</sub> respectively. During the carbonation-calcination cycles the CO<sub>2</sub> gas concentration at the outlet stream was measured with a Guardian Plus equipment in the range 0 - 30 ± 0.75 % (mild calcination conditions) or 0 - 100 ± 2 % (more realistic calcination conditions). The oven temperature was controlled by an Eurotherm® 2000 series equipment and the temperature inside the quartz reactor was monitored by a thermocouple type K. Labview software interface was used for data acquisition.

The sorbent sample (2 g) was loaded into the reactor and pre-calcined at 800 °C under N<sub>2</sub> atmosphere until the CO<sub>2</sub> release stopped (mild calcination conditions) or 930 °C during 15 min under 80% of CO<sub>2</sub>

balanced in N<sub>2</sub>, followed by N<sub>2</sub> atmosphere until the CO<sub>2</sub> release stopped for ensuring the sorbent complete decarbonation. After this activation step, the temperature was cooled down to 700 °C and the carbonation step was conducted with a feed stream of 15 % v/v of CO<sub>2</sub> (150 ml/min of CO<sub>2</sub> in N<sub>2</sub> balance, to simulate a realistic CO<sub>2</sub> concentration in the flue gases) until stabilization of the outlet stream CO<sub>2</sub> concentration, which means that the sorbent reached its maximum CO<sub>2</sub> capture capacity. After carbonation, the CO<sub>2</sub> feed flow was stopped and the sample was heated up to 800 °C under pure N<sub>2</sub> flow (mild calcination conditions) or heated up to 930 °C for 15 min, under 80% of CO<sub>2</sub> balanced in N<sub>2</sub> (more realistic calcination conditions) followed by a pure N<sub>2</sub> flow. Then the sample was cooled down to 700 °C for starting a new carbonation-calcination cycle. To determine the textural and structural changes of CaO based sorbents, experimental CaL tests were stopped (e.g. after 2, 5, 10 and 20 cycles) and the calcined sorbents were collected and immediately analysed by N<sub>2</sub> sorption and XRD technique. For comparative reasons, an experimental test only including the pre-calcination (0 cycles) was performed under mild calcination conditions, i.e. after the sorbent activation, the experiment was stopped, and the calcined sorbent collected and characterised.

The amount of CO<sub>2</sub> captured (moles) in each carbonation step,  $n_{CO_2,carb}$ , was estimated by equation 1:

$$n_{CO_2,carb} = \int_{t_1}^{t_2} (n_{CO_2,i} - n_{CO_2,not\ capt}) dt \quad (\text{Eq.1})$$

Where  $n_{CO_2,i}$  and  $n_{CO_2,not\ capt}$  are, respectively, the molar amount of CO<sub>2</sub> fed to the reactor and the molar amount of CO<sub>2</sub> gas that did not react, measured in the off-gas during carbonation, between carbonation time t<sub>1</sub> and t<sub>2</sub>. The CaO conversion along the carbonation-calcination cycles was determined by equation 2:

$$CaO\ conversion = \frac{n_{CO_2,carb} \times M_{CaO}}{m_{sorbent} \times w_{CaO}} \times 100 \quad (\%) \quad (\text{Eq.2})$$

where  $M_{CaO}$  is the molar mass of CaO,  $m_{sorbent}$  is the initial mass of the sorbent and  $w_{CaO}$  is the percentage of CaO in the initial mass of the sorbent. The CaO content was estimated through elemental chemical analysis of the fresh materials.

### 3. RESULTS AND DISCUSSION

#### 3.1. Sorbents characterization

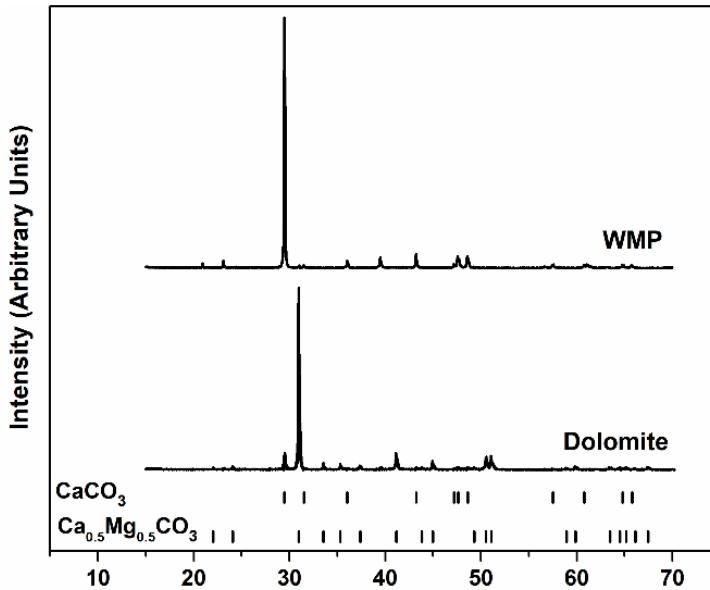
The chemical elemental analysis of the WMP and dolomite sorbent samples, dried at 120 °C, is presented in table 1.

**Table 1.** Chemical elemental composition of fresh WMP and dolomite sorbents dried at 120 °C

Fresh sorbent	Elemental Content (wt. %)					
	Ca	Mg	Al	Fe	Si	C
WMP	38.5	0.37	0.06	0.05	0.51	11.9
Dolomite	24.9	10.3	0.01	0.01	0.04	12.6

The results show that the WMP, like the limestone's rocks, is mainly composed by calcium and carbon. ASTM C119-16 [31] classifies limestone and marble in different groups of rocks, marble is a carbonate rock that has acquired a distinctive crystalline texture by recrystallization, most commonly by high heat and pressure during metamorphism, and is mainly composed by the carbonate minerals calcite and dolomite, individually or in combination. Dolomite belongs to the limestone group and contains two main elements in its composition: Ca and Mg. A ratio of Ca/Mg (wt. %) of 2.4 was obtained, so this sorbent is classified as a calcitic dolomite [32]. Comparatively with the WMP, lower amounts of Si, Al and Fe were found in dolomite.

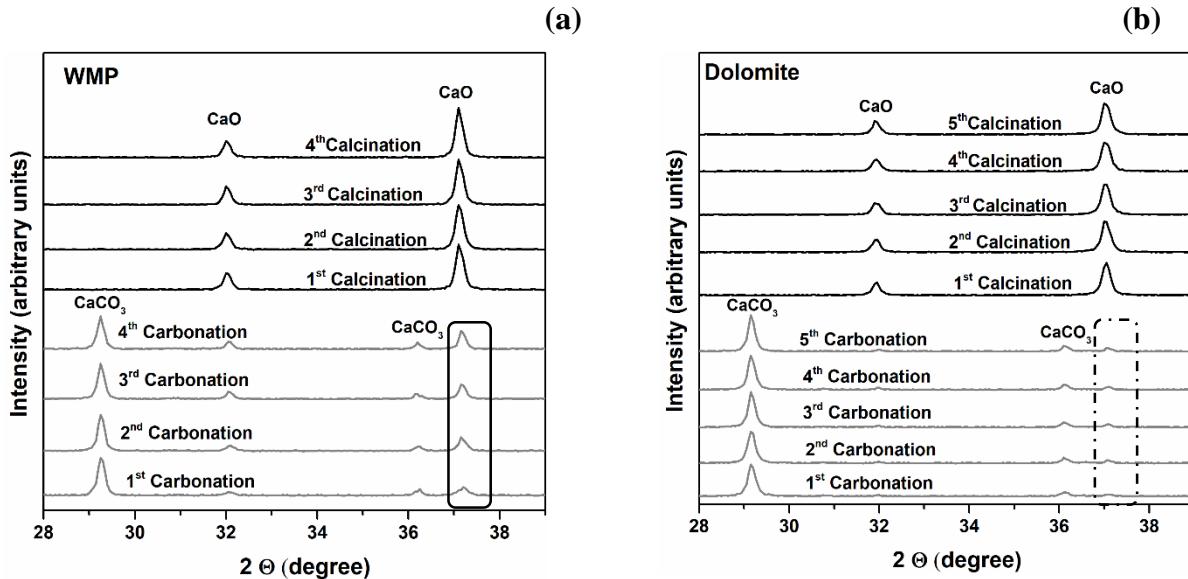
XRD measurements were performed to identify the sorbent samples phases. The XRD diffractograms of the fresh sorbents dried at 120 °C are presented in Fig. 2.  $\text{CaCO}_3$  is the main compound of WMP, which is in agreement with its chemical composition. For dolomite, the main phase is  $\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3$  (78%), followed by  $\text{CaCO}_3$  (22%), which evidences that besides the dolomite phase, this sorbent also contains some isolated calcite ( $\text{CaCO}_3$ ).



**Fig. 2.** XRD patterns of the fresh sorbents dried at 120 °C

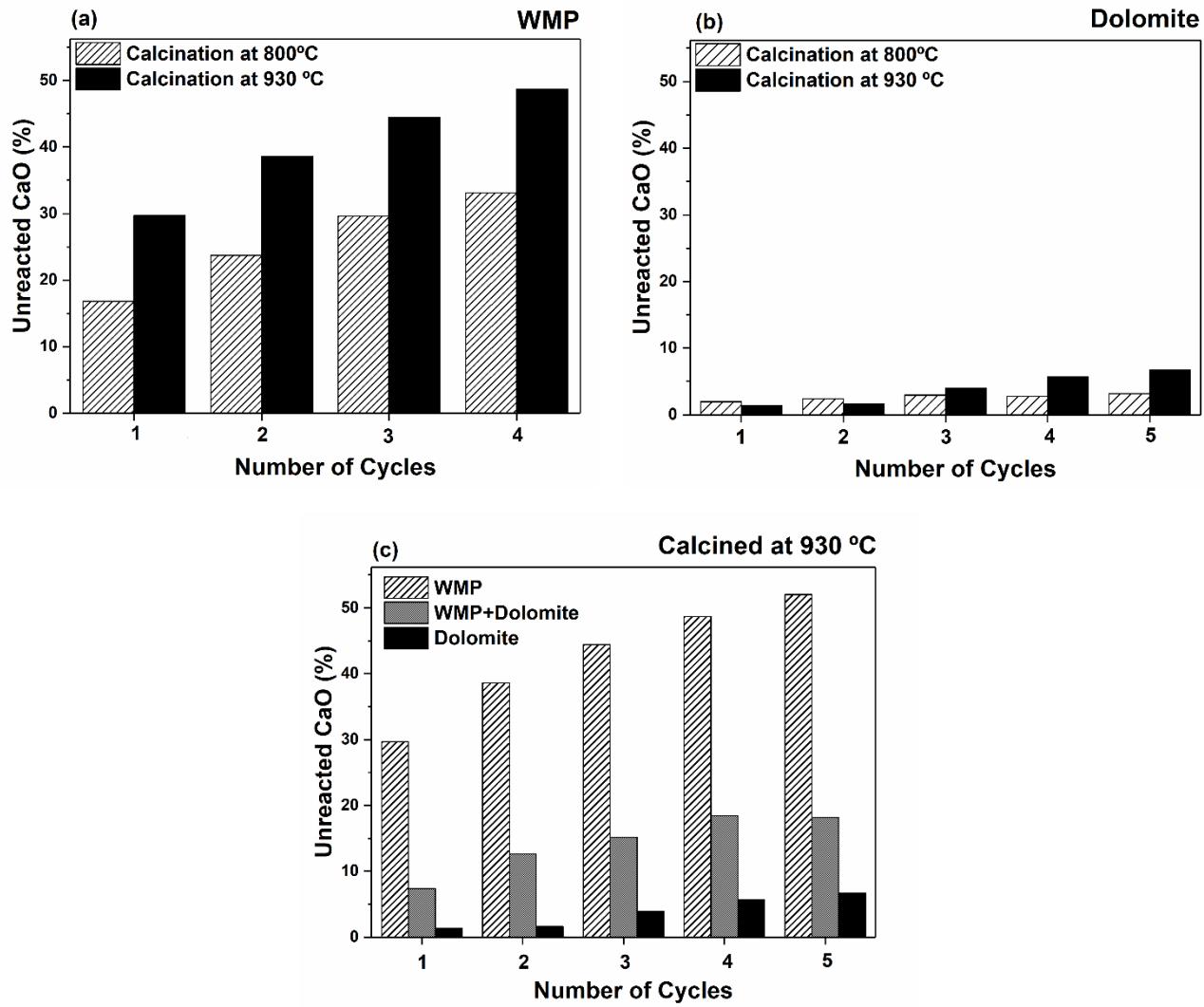
### 3.2. Evaluation of sorbents reactivity by *in-situ* XRD

The carbonation – calcination cycles using WMP and dolomite as sorbents were performed at an *in-situ* XRD chamber and the evolution of CaCO<sub>3</sub> and CaO crystallite phases present in each one of the materials samples was recorded in the XRD diffractograms in the range 28 and 39 ° in 2θ. Fig. 3 (a) and (b) show results obtained when the calcination is performed under N<sub>2</sub> at 800°C. In the case of WMP (Fig 3 (a)), the relative amount of CaO that is not converted to CaCO<sub>3</sub> at the end of the carbonation stage increases with the number of carbonation cycles (black rectangle line). However, in the case of dolomite (Fig. 3 (b)), the amount of CaO that is not carbonated after the carbonation stage (dotted line rectangle), though increasing, is less significant.



**Fig. 3.** *In-situ* XRD diffractograms of WMP (a) and dolomite (b) obtained along the carbonation-calcination cycles: carbonation with 15% of CO<sub>2</sub> at 700°C and calcination with 100% of N<sub>2</sub> at 800°C

To evaluate the effect of the calcination temperature on the activity of WMP and dolomite sorbents CaO carbonation, the calcination steps were performed under mild and more realistic calcination conditions, i.e., at 800 and 930°C, respectively. The amount of unreacted CaO during carbonation, based on the relative amount of CaCO<sub>3</sub> and CaO, was obtained from Rietveld refinement for both temperatures, considering only CaO and CaCO<sub>3</sub> phases between 28 and 39 ° in 2θ. As shown in Fig. 4 (a) and (b), in general, the amount of unreacted CaO during the carbonation step increases for both sorbents when a higher calcination temperature is used, confirming that the increase from 800 to 930°C favours the sorbents loss of activity. In case of dolomite, during the 1<sup>st</sup> and 2<sup>nd</sup> cycles, the unreacted CaO is very similar for both temperatures, which can be justified by the lack of accuracy near XRD quantification limits. Considering the 4<sup>th</sup> carbonation as reference, it was verified that the percentage of unreacted CaO between 800 and 930 °C increase 50% and 102% for WMP and dolomite, respectively, evidencing that the dolomite sorbent skeleton/microstructure suffers more changes in this range of temperatures than the WMP. Anyway, the fraction of unreacted CaO in dolomite during carbonation step is lower than in WMP, meaning that the carbonation during the Ca-looping is more efficient for dolomite than for WMP, maybe because the MgO hinders the sintering of CaO [30].



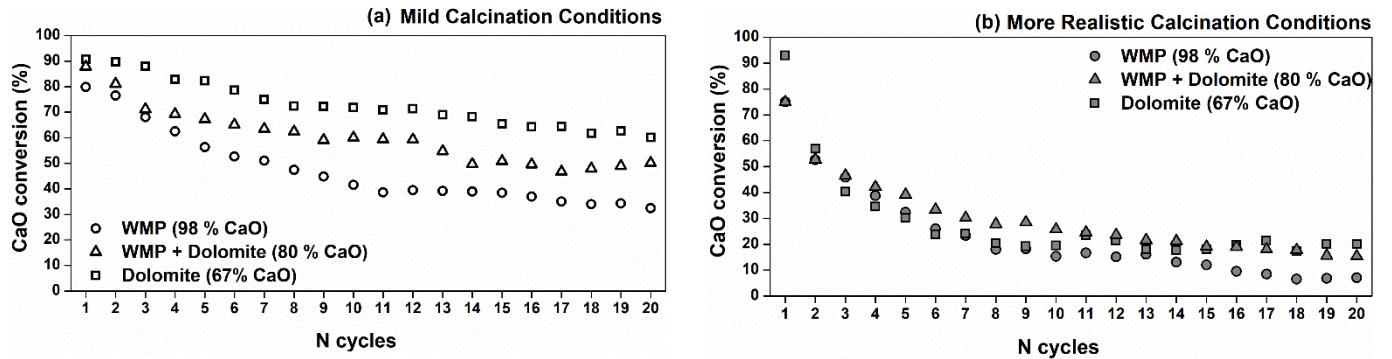
**Fig. 4.** Amount of unreacted CaO (%) during the carbonation step with 15% of CO<sub>2</sub> at 700°C, and calcination with 100% of N<sub>2</sub> at 800°C (mild conditions) or 80% of CO<sub>2</sub> at 930 °C (more realistic conditions): (a) WMP, (b) dolomite; and (c) WMP, dolomite and a blend of WMP and dolomite with 80% of CO<sub>2</sub> at 930 °C

Since the MgO present in the sorbent is expected to hinder the CaO sintering, a preliminary test was carried out at 930 °C with a blend of WMP and dolomite (80% CaO and 20% of MgO in a calcined basis) aiming to improve the WMP sorbent carrying capacity, and the results are compared with the individual sorbents. As can be observed in Fig.4 (c), the blend of WMP +dolomite seems to be a promising approach to improve the sorbents activity, since after 5 cycles the amount of unreacted CaO in the blend sample is much lesser (19%) than in pure WMP (52%). It should be highlighted that the results obtained by *in-situ* XRD studies are important to predict tendencies and compare sorbents

carrying capacity, but when compared with results attained using different methodologies, like the fixed bed reactor, some differences can be observed due to heat transfer and diffusional limitations that occur more intensively in this type of apparatus, whose results will be shown in the next section.

### 3.3. Evaluation of sorbents reactivity for CO<sub>2</sub> capture under different calcination conditions

WMP and dolomite sorbents were tested in a fixed bed reactor CaL unit under mild (N<sub>2</sub>, at 800°C) and more realistic (80%CO<sub>2</sub>, 930°C) calcination conditions, for evaluation of their cyclic CO<sub>2</sub> capture performance. As an approach to improve the stability and the CO<sub>2</sub> carrying capacity of WMP sorbent, a blend of WMP + dolomite sorbent was also tested. Fig. 5 shows the CaO conversion (%) for 20 carbonation/calcination cycles for all the sorbents using mild (5.a) or more realistic (5.b) calcination conditions. The sorbents' CaO conversion was obtained based on the chemical composition of the sorbents (table 1) and its CaO content because, under the used experimental conditions, MgO was shown to be inert [28, 33]



**Fig. 5.** CaO conversion of WMP, dolomite and WMP/dolomite blended sorbent after 20 cycles of carbonation at 700 °C and calcination under (a) mild:800°C and 100% of N<sub>2</sub>, or (b) more realistic: 930°C and 80% of CO<sub>2</sub> calcination conditions

As expected, at mild calcination (Fig. 5.a), dolomite sorbent with ca. 33% MgO (calcined basis), presents a higher initial CaO conversion on the 1<sup>st</sup> cycle, ca. 91 %, and for WMP it is ca. 80 %, but after 20 cycles, the dolomite CaO conversion is approximately double that of the WMP CaO conversion, i.e. 60 and 32%, respectively. The results show that the CaO content in the sorbent sample is not the most relevant factor, and due to the presence of other chemical elements (e.g. Mg), comparatively with WMP, an improved CaO conversion is achieved for dolomite sorbent. A blend of WMP and dolomite (80 % of CaO and 20 % of MgO in calcined basis) was also prepared and tested for 20 cycles. An increase in CaO conversion was obtained with the increase of MgO content in the blended sorbent, i.e., the CaO conversion increased from 32% in WMP to 50% for the blended sorbent. The sorbents stability

(considering the 1<sup>st</sup> cycle CaO conversion as reference), after 20 cycles, was also evaluated and the deactivation was 59, 41 and 34% respectively for WMP, WMP + dolomite blend and dolomite. Figure 5 shows that the sorbent deactivation is directly related with the MgO content (calcined basis) in the sorbents: 1% in WMP, 20 % in the blended sorbent and 33% in dolomite. It is well known that MgO does not undergo carbonation under typical CaL conditions, but it provides additional pore volume during the dolomite calcination. Also, the high Tammann temperature (1276 °C) for MgO, allows the stabilization of the pore structure of dolomite [23, 34].

It is generally accepted that carbonation of CaO grains occurs through two differentiated phases consisting of a fast reaction-controlled stage followed by a much slower solid-state diffusion stage.

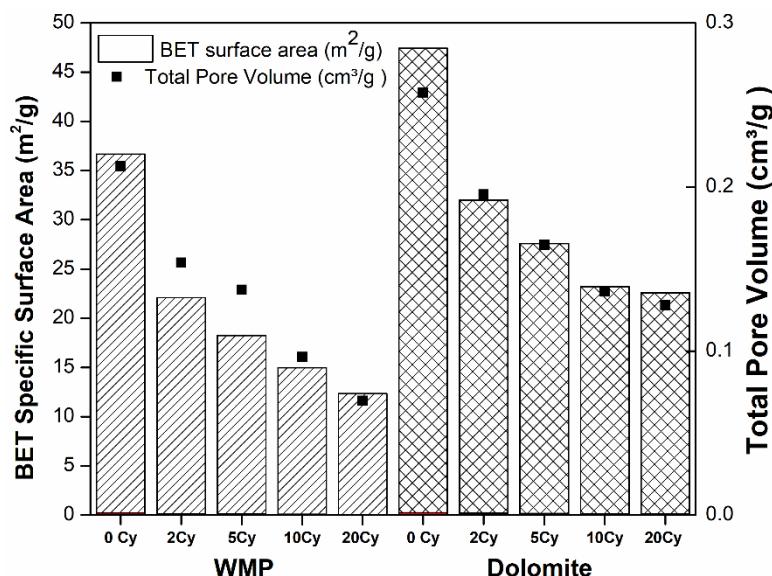
Recent studies [30] have shown that the improved CO<sub>2</sub> capture capacity of dolomite is mostly due to the greatly promoted carbonation in the solid state diffusion phase. Solid state diffusion is promoted by impurities and lattice defects, hence the nanocrystalline CaO grains and the presence of MgO inert grains in calcined dolomite favour carbonation in the solid-state diffusion-controlled phase. At the usual non-realistic mild calcination conditions reported in literature, the improved performance of dolomite with the increasing number of cycles, can be attributed to the stabilizing effect of the inert MgO skeleton which hinders the aggregation and subsequent sintering of the CaO crystals during the CaCO<sub>3</sub>/CaO transformation.

In the present study the same three sorbents were also tested for 20 cycles under the above mentioned more realistic calcination conditions and the CaO conversion (Fig. 5.b) was compared with the one attained under mild calcination conditions (Fig 5.a). It was observed that the sorbents' CaO conversion is much lower when more realistic calcination conditions were used, but the three sorbents present a similar performance and the differences between the sample's deactivation are quite low along the first 10 cycles. It is interesting that Figure 5.b) shows that in the case of more realistic calcination conditions, the blended sorbent WMP + dolomite achieved a CaO conversion of 20% after 20 cycles which is higher than the corresponding CaO conversion observed for dolomite of 15% and for WMP of 7%. Therefore, under more realistic calcination conditions with 80% CO<sub>2</sub> at 930 °C, the CaO conversion is much lower, even for dolomite sample, but there is a stronger synergetic effect of inert MgO grains of calcined natural dolomite in the blend WMP + dolomite sorbents that leads to an improved stability along the cycles when compared with both WMP and dolomite used separately as sorbents. The MgO from dolomite should hinder the CaO sintering. The comparison of the sorbents' performance under mild and more realistic calcination conditions shows that the higher temperature that is required at real industrial calcination conditions, due to the high concentration of CO<sub>2</sub> in the calciner, significantly affects the

sorbents' performance. Moreover, the expected realistic sorbents' performance under industrial operating calcination conditions, can be very different from the typical results found in the literature in experimental research tests using CaL sorbents which are usually tested using mild calcination conditions under N<sub>2</sub> or air atmospheres, not realistic from an industrial point of view and far from the real ones. This conclusion reinforces the need for more studies under real calcination conditions, i.e., under high CO<sub>2</sub> concentration with different types of sorbents blends of solid wastes such as wastes of marble powder and cheap natural dolomite to supply streams with high concentration of CO<sub>2</sub> at the exit of the calciner more appropriate for subsequent CO<sub>2</sub> conversion processes application.

### 3.4. Textural properties of sorbents tested under mild and more realistic calcination conditions

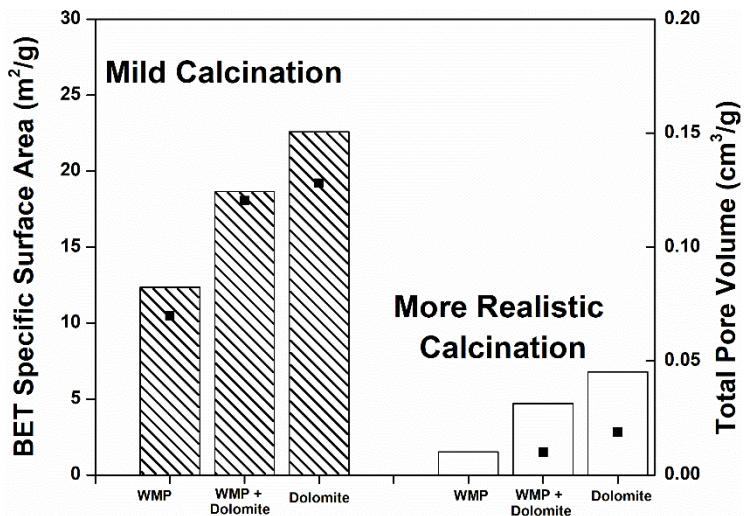
The textural properties of the WMP and dolomite samples cyclically tested under mild calcination conditions were evaluated. The samples were collected from the fixed bed unit after n carbonation-calcination cycles (n=2, 5, 10 and 20) and the corresponding textural properties were correlated with CaO conversion data. Due to the hygroscopic properties of CaO, which can be easily converted to Ca(OH)<sub>2</sub> in the presence of atmospheric moisture, the used samples were removed from the reactor for characterization before cooling down to room temperature, avoiding changes in their composition and textural properties. S<sub>BET</sub> and V<sub>p</sub>, were determined for both sorbent samples used after n cycles (n=0, 2, 5, 10 and 20) and the results are presented in Fig. 6.



**Fig 6.** S<sub>BET</sub> and V<sub>p</sub> for WMP and dolomite samples after carbonation-calcination cycles under mild conditions.

The  $S_{BET}$  reduction from the sorbent activation (0 cycles) to 20 cycles was 66 and 52% for WMP and dolomite, respectively. The higher initial values of  $S_{BET}$  and  $V_p$  and the lower reduction of  $S_{BET}$  of dolomite sorbent along the carbonation-calcination cycles comparatively with the WMP agree with the CaO conversion values observed in Fig. 5.a. For both sorbents, the  $S_{BET}$  decreases along the cycles, as expected, but this decrease, due to the loss of particles porosity, is more significant for WMP than for dolomite in agreement with the higher deactivation rate of WMP (59%) comparatively with dolomite (34%) during the experiments carried out in the fixed bed. As reported in literature [35], the higher stability of certain sorbents is justified by the presence of additional oxides that act as inert support and reduce the neck blockage associated to the sintering mechanisms. According to the Rule of Tammann, sintering due to lattice diffusion is generally observed at temperatures above  $0.5T_m$ , where  $T_m$  is the melting temperature (in Kelvin). Nevertheless, surface diffusion is already expected to occur above  $0.33T_m$  (Hüttig Temperature) [36]. For CaO,  $T_{\text{Tammann}}$  and  $T_{\text{Hüttig}}$  are 1170 and 679 °C, respectively, which means that the sintering process should occur essentially due to surface diffusion and could even start during the carbonation carried out at 700 °C. Ideally, to work as inert supports, the oxides present in CaO-based sorbents should have a melting temperature higher than that of CaO. In the case of the oxides identified in the calcined WMP and dolomite (table 1), only MgO has a melting temperature higher than CaO, i.e. 2800 °C, which means it is an inert support suitable for this reaction, so the considerable amount of Mg (table 1) in natural dolomite, comparatively to WMP, justifies the lower sintering of this sorbent. Hu *et al.* [35] studied several inert supports and Mg-based supports were classified as good candidates to minimize the sintering process, as well as the Al-based support materials. On the other hand, Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> should not be desirable, attending to their lower melting temperatures (respectively, 1565 and 1730 °C), which means that the  $T_{\text{Tammann}}$  of Fe<sub>2</sub>O<sub>3</sub> is 646 °C and of that of SiO<sub>2</sub> is 729 °C.

The  $S_{BET}$  and  $V_p$  of sorbents WMP, dolomite and WMP + dolomite blend, tested under mild (at 800 °C, under N<sub>2</sub>) and under more realistic (at 930 °C, under 80% CO<sub>2</sub>) calcination conditions for 20 cycles are showed in Fig. 7.



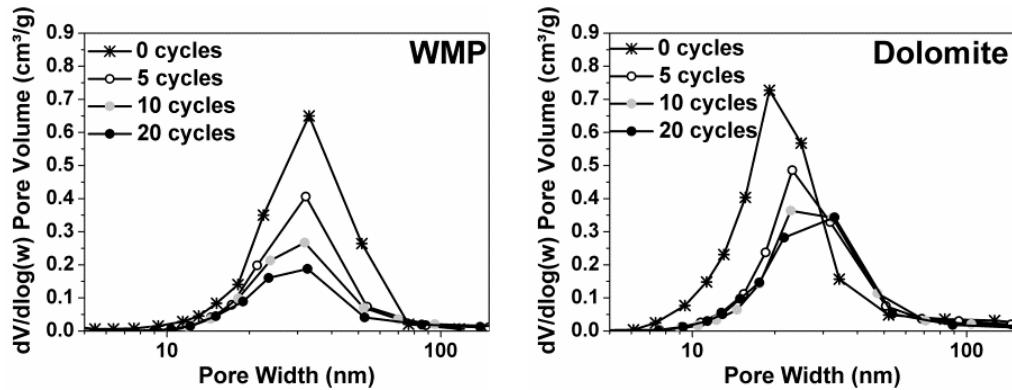
**Fig. 7.** S<sub>BET</sub> and V<sub>p</sub> for sorbents WMP, dolomite and WMP + dolomite blended, after 20 cycles, under mild (800°C and 100% of N<sub>2</sub>) and more realistic (930°C and 80% of CO<sub>2</sub>) calcination conditions

Fig. 7 shows that the calcination conditions during CaL cycles drastically affect the final S<sub>BET</sub> and V<sub>p</sub> of the sorbent samples. The S<sub>BET</sub> of the three sorbents after 20 cycles decreases between 70 and 88% when comparing the mild calcination conditions with the more realistic calcination conditions, thus explaining the results obtained for the CaO conversion decrease observed in Fig. 5. Taking into account that the T<sub>Hüttig</sub> of CaO (679 °C) and MgO (741 °C) were largely exceeded, it can be considered that the sintering process due to solid-state diffusion that occurs in the calcination stage is enhanced at the higher temperature (930 °C) of the more realistic calcination necessary to produce a concentrated stream of CO<sub>2</sub> (80%) than under mild calcination at 800 °C.

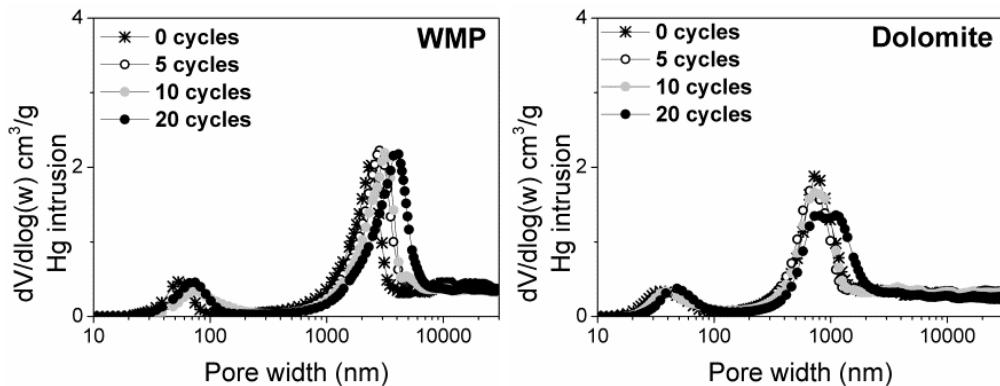
Under mild calcination conditions, the WMP + dolomite blended sorbent (ca. 20% of MgO in the calcined sample) presents a higher S<sub>BET</sub> and V<sub>p</sub> than the WMP sorbent (ca. 1.1% of MgO in calcined sample), so, it can be seen that the high concentration of MgO in the blended sorbent favored an increase of ca. 51% of the S<sub>BET</sub>, in agreement with the higher CaO conversion observed in Fig. 5.a. Under realistic calcination conditions the blended sorbent also presents a higher S<sub>BET</sub> than the WMP, i.e., the S<sub>BET</sub> of blended sorbent increases 212%. It was observed that the S<sub>BET</sub> of WMP decreases abruptly when the mild calcination conditions are replaced by the realistic one, due the low sintering resistance of this sorbent at higher temperatures.

The pore size distribution (PSD) of sorbents tested under mild calcination conditions was estimated using BJH model (desorption branch of the isotherm). Fig. 8 shows that the average pore width is mainly within the range of mesopores (2-50 nm). Dolomite has a total pore volume higher (0.72 and 0.30 cm<sup>3</sup>/g

for 0 and 20 cycles, respectively) than WMP ( $0.64 \text{ cm}^3/\text{g}$  and  $0.18 \text{ cm}^3/\text{g}$  for 0 and 20 cycles, respectively) in agreement with the higher CaO conversions of dolomite. Nevertheless, the average pores width of WMP is almost constant along the carbonation-calcination cycles (ca. 30 nm), while, for dolomite, the average pores width increases along the cycles, i.e. for 0 cycles the average pore size was 19 nm and then the smaller pores disappeared along the cycles and the average pore size became 30 nm after 20 cycles. The observed PSD profiles can be related with the sintering resistance of WMP and dolomite. In the case of WMP, the sintering of CaO particles causes mesopore volume reduction, without the formation of intermediate large mesopores. However, since dolomite is a sorbent more resistant to sintering due to the presence of MgO, the formation of intermediate size mesopores occurs, with an increasing average pore width along the carbonation-calcination cycles.



**Fig. 8.** Pore size distributions obtained from  $\text{N}_2$  adsorption-desorption technique (PSD from BJH desorption branch) for WMP and dolomite after 0, 5, 10 and 20 carbonation-calcination cycles under mild calcination conditions (calcination at  $800^\circ\text{C}$  and 100% of  $\text{N}_2$ )

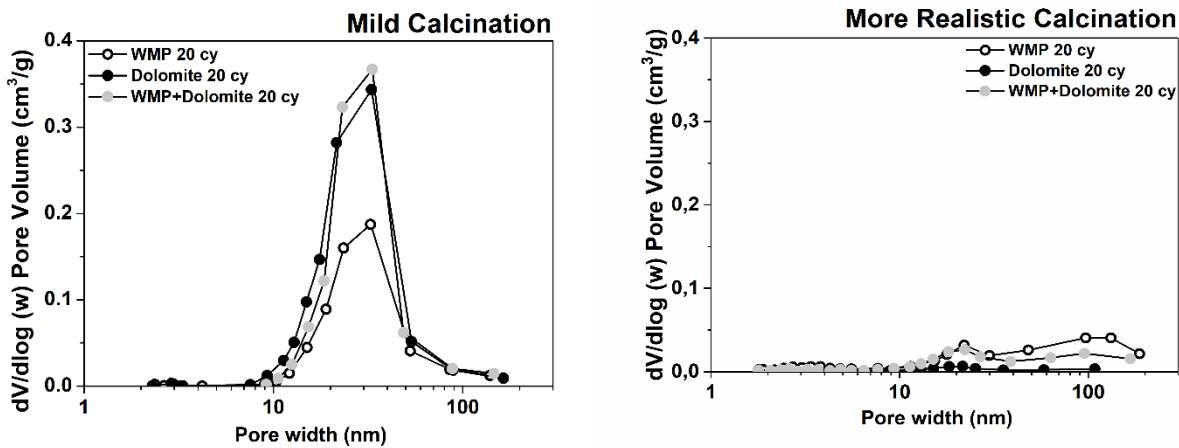


**Fig. 9.** Pore size distributions obtained from Hg porosimetry technique for WMP and dolomite after 0, 5, 10 and 20 carbonation-calcination cycles under mild calcination conditions (calcination at  $800^\circ\text{C}$  and 100% of  $\text{N}_2$ )

The Hg porosimetry technique was also used to complete the average pores size distribution in the macropores region (Fig. 9). The PSD curves obtained by Hg porosimetry technique (Fig.9) show that WMP and dolomite present a bimodal pores size distribution and confirmed the presence of meso and macropores for all samples. Both sorbents show a slight increase of the average macropore width along the cycles, which can be related with the particles sintering, especially in the case of WMP. For similar Hg intrusion volumes, the average pore width for WMP is around 1200 nm and for dolomite it is around 800 nm, which is in agreement with the conversion of each sorbent, i.e. lower pore width contributes to a higher  $S_{BET}$  improving the  $\text{CO}_2$  capture capacity.

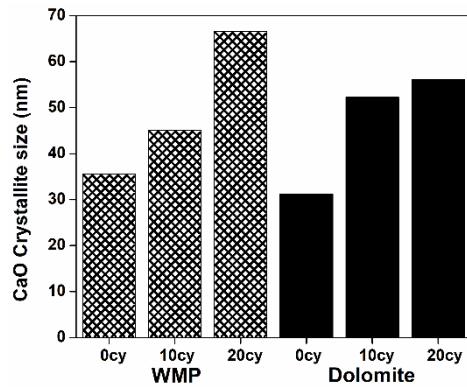
Fig. 10 compares the PSD curves of the sorbents tested under mild and more realistic calcination conditions. It can be seen that the higher temperature of the more realistic conditions results in a significant drop of the pore volume content of all sorbents.

At more realistic calcination conditions, the WMP sorbent presents an interesting behaviour: the pore volume content also decreases significantly, but unlike the dolomite, it maintains a small amount of mesopore volume content near an average size of 20-30 nm. This is probably related to the geological formation of marble that is a metamorphic rock, meaning that this WMP sorbent is formed under high pressure and temperature, which can explain its higher resistance to mesopore volume reduction, comparatively with dolomite that is a sedimentary rock. This effect is also observed in the blended sorbent that, due to some WMP content, also presents a content of mesopores slightly higher than dolomite. Although WMP sorbent has a higher mesopore and small macropore volume content, dolomite and the blended sorbent present a higher  $\text{CaO}$  conversion at more realistic calcination conditions, showing that the  $S_{BET}$  should have a crucial role in  $\text{CaO}$  conversion (Fig.7).



**Fig. 10.** Pore size distributions obtained from  $N_2$  adsorption-desorption technique (PSD from BJH desorption branch) for WMP, dolomite and WMP/dolomite mixed sorbent, after 20 cycles, under mild ( $800^\circ\text{C}$  and 100% of  $N_2$ ) and more realistic ( $930^\circ\text{C}$  and 80% of  $\text{CO}_2$ ) calcination conditions.

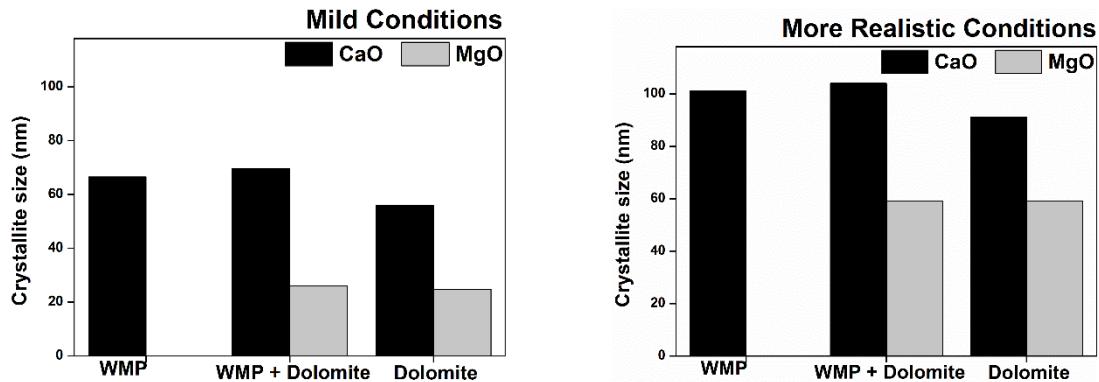
The average crystallite size of the used sorbents was assessed by Scherrer's equation from XRD data. Fig. 11 shows that, even under mild calcination conditions, the average size of CaO crystallites increases 87 and 79 % between 0 and 20 cycles for WMP and dolomite, respectively. Nevertheless, for dolomite the average CaO crystallites size almost stabilized from the 10<sup>th</sup> cycle on, maybe due to the presence of MgO that should limit the CaO crystallites growth, indeed between the 10<sup>th</sup> and 20<sup>th</sup> cycle the crystallites size increases only ca. 7%.



**Fig. 11.** Average crystallite size (nm) for WMP and dolomite after 0, 10 and 20 carbonation-calcination cycles under mild calcination conditions ( $800^\circ\text{C}$  and 100% of  $N_2$ )

A growth in the CaO crystallites size when the number of carbonation-calcination cycles increases, meaning more calcination time, was also observed by Biasin *et al.* [12] who verified that, by using a constant calcination temperature ( $900^\circ\text{C}$ ), the CaO crystallites size increased 390% when the calcination time increased from 5 to 60 min.

Fig. 12 shows that more realistic calcination conditions lead to the increase of the average crystallites size of all sorbents. After 20 cycles, the CaO crystallite size increases 49, 52% and 62%, for WMP + dolomite blend, WMP and dolomite, respectively. For dolomite, the CaO crystallites size increase was more accentuated because, under more realistic calcination conditions, this sorbent lost the MgO *protective* effect that acts as physical barrier between CaO particles, since at 930°C the  $T_{\text{Hüttig}}$  of MgO (ca. 741 °C) was largely exceeded. In the case of blended sorbent, the increase of CaO crystallite size was 49%, which can be explained by the synergistic effect of different textural parameters of blended sorbents. Fig. 10 shows that at higher calcination temperatures (930 °C), the WMP is more resistant to mesopores reduction than dolomite, maybe due to the rock formation genesis (metamorphic vs. sedimentary). So, it is expected that the CaO crystallites of WMP + dolomite sorbent take advantage of the WMP mesopores reduction resistance at higher calcination temperatures (930 °C) and since the blended sorbent contains less MgO than the dolomite (20% vs. 33%), the MgO *protective* effect was less sharp in the blended sorbent.



**Fig. 12.** Average crystallite size (nm) for WMP, dolomite and WMP+dolomite mixed sorbent, after 20 cycles, under mild (800°C and 100% of N<sub>2</sub>) and more realistic (930°C and 80% of CO<sub>2</sub>) calcination conditions

Fig. 12 also shows that the MgO crystallites were strongly affected by the calcination conditions, i.e., an increase in the average crystallites size of ca. 126% was observed when more realistic calcination conditions were used. Anyway, the presence of MgO crystallites in the sorbent is still useful since they contribute to a higher separation between the CaO crystallites, hindering their sintering, and an improved CaO conversion along the carbonation-calcination cycles can be achieved (Fig. 5).

Valverde *et al.* [37-38] studied in detail the increase of CaO crystallites size and correlated it with the CO<sub>2</sub> partial pressures used during the calcination step. For CO<sub>2</sub> partial pressures near the equilibrium (P/P<sub>eq</sub> ~ 1), the calcination occurs slowly and a metastable CaO\* phase will contribute to the CaO

nanocrystals agglomeration and crystallite size increase. In this case, the crystallites could reach the maximum value of 1000 nm [18] and the agglomeration is considered the main mechanism for the crystallites growth and sorbent deactivation. For low CO<sub>2</sub> partial pressures ( $P/P_{eq} \ll 1$ ), desorption and structural transformation occur rapidly, and the calcination rate is limited by chemical decomposition, so the metastable CaO\* phase is present for very short times, which hinders the growth of CaO crystallites by agglomeration. In that case, sintering is considered the main mechanism of crystallite growth and usually the crystallites grow only until 50 nm. Besides the CO<sub>2</sub> calcination partial pressure, the calcination temperature has also a relevant role in the CaO sintering. Abass et al. [39] evaluated the effect of CaCO<sub>3</sub> decomposition temperature on the average CaO crystallites size and verified that it increases ca. 121-129 % when the temperature increased from 800 to 1000 °C, this increase is higher than the observed in Fig. 12 for CaO crystallites, however the range of calcination temperature used in the present work is smaller (800-930 °C). For the sorbents evaluated in the present work, the crystallites size increase should be explained by both factors: CO<sub>2</sub> partial pressure and calcination temperature.

#### 4. CONCLUSIONS

The use of cheap natural materials based on marble powder wastes and natural dolomite as sorbents for the CO<sub>2</sub> capture is extremely appealing to make CaL technology a more sustainable and eco-friendly process. Furthermore, for the downstream utilization of CO<sub>2</sub> at an industrial scale, it is more convenient that the sorbents calcination during CaL process occur under a concentrated CO<sub>2</sub> flow, which implies higher calcination temperatures (> 900 °C). However, these conditions are rarely found in literature in experimental research tests, especially using natural sorbents and laboratory scale reactors.

In this work the CO<sub>2</sub> capture performance of natural CaCO<sub>3</sub>-based wastes such as WMP (a waste generated by the marble producers in large quantities in Portugal 250-400 ton/year), of a natural dolomite (which is a cheap and abundant CaO natural precursor), and of a blend of WMP + dolomite, was studied and compared for Ca-L multiple carbonation-calcination cycles using mild (800 °C, N<sub>2</sub>) and more realistic (930 °C, 80% CO<sub>2</sub>) calcination conditions. The synergetic effect of blending WMP and natural dolomite due to the high amount of CaO in the WMP and to the barrier effect provided by the presence of MgO in calcined dolomite, is also assessed as an approach to tailor cheap wastes-based blended sorbents with improved carrying capacity and stability along the cycles even under realistic calcination conditions.

Under mild calcination conditions, the results show that after 20 cycles, the deactivation of WMP and dolomite was 59 % and 34 % respectively, and comparatively with the WMP a positive effect on the blended sorbent carrying capacity was reached, whose deactivation was 41%. The results were supported by the textural properties of the sorbents, which evidenced an improved SBET of the blended sorbent comparatively with the WMP, due to the higher MgO content in the blended sorbent (20 vs. 1.1 % in calcined basis).

Although in the case of using more realistic calcination conditions the sorbents deactivation after 20 cycles is higher when compared with the deactivation observed at mild calcination conditions, interesting promising results were found when using a blended sorbent of WPM + natural dolomite. Under more realistic CaL operation conditions, as regards calcination under high CO<sub>2</sub> concentration at high temperature, there is a stronger synergetic effect of inert MgO grains of calcined natural dolomite in the blended WMP + dolomite sorbent that leads to an improved stability along the cycles when compared with both WMP and dolomite used separately as sorbents. The differences of the sorbents carrying capacity, under mild and more realistic calcination conditions, can be explained by the CaO and MgO Hüttig temperature, that are 679 and 741°C respectively, which means that under more realistic calcination conditions (930 °C), even for the MgO, this critical temperature was largely exceeded and the sintering process due to surface diffusion is much more accentuated. Blending WMP with natural dolomite is found as a promising approach to tailor cheap wastes-based blended sorbents with improved carrying capacity and stability along the cycles even under realistic industrial scale calcination conditions.

Since WMP is a waste generated in large amounts in quarrying marble industry, the use of WMP resources as CaO precursors in blended sorbents with natural dolomite, which is also a cheap and abundant CaO precursor, seems a promising and economically attractive option to the circular economy concept and should be encouraged as a bi-ecofriendly material for the CaL process due to the advantages of contributing to reduce the cost of the CaL cycle CO<sub>2</sub> capture process, as well as to minimizing the adverse environmental impacts of the high volume of WMP generated.

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: