ABSTRACT: There are currently no studies in the literature on the use of natural waste marble powder (WMP) resources as inexpensive sorbents for looping cycle CO₂ capture. The high volume of marble production is associated with considerable amounts of WMP generated as byproduct during cutting and polishing procedures, which negatively impacts the surrounding environment. The main goal and innovative idea addressed in this study consists of investigating if solid wastes WMP from marble producer sources can be used as possible inexpensive and effective solid materials to be used as precursors of CaO-based sorbents in Ca-looping cycle CO₂ post-combustion capture process. The cyclic carbonation–calcination reactions were experimentally studied in a laboratory-scale fixed-bed reactor unit for 10 and 20 cycles. The innovative and interesting results obtained show that Portuguese WMP represents a category of promising natural inexpensive solid sorbents to be used as effective CaO-based sorbents for looping cycle CO₂ post-combustion capture, because of their increased CO₂ carrying capacity and better cyclic stability with lower sorbent deactivation with the number of cycles, when compared with commercial CaCO₃ reference sorbent precursor and with other natural and synthetic CaO-based sorbents, and other CaO-solid-based materials from industrial and natural wastes recovery, reported in the literature. The WMP resources have potential to be an economically attractive option thus contributing to reduce the cost of the Ca-looping cycle CO₂ capture process, as well as to minimize the adverse environmental impacts of the high volume of WMP generated in the marble producers.

1. INTRODUCTION

In 2010, the world emitted ~31.8 Gt of CO₂ due to energy consumption and ~145 Gt of CO₂ must be captured and stored or reused from 2010 to 2030.¹

The European Commission defined ambitious targets concerning CO₂ emissions reduction, stating that this can only be achieved with the implementation of carbon capture and storage (CCS) technologies. CCS is a viable method to reduce in-depth CO₂ emissions from cement manufacture, because of the very high concentration of CO₂ in the flue gas (~13%–33%, compared with ~3%–13% in power plants).²,³

One of the most promising CCS post-combustion technologies is the “calcium looping cycle” (Ca-looping cycle) process, which endeavors to scrub CO₂ from flue gases by using CaO-based sorbents, and which appears to potentially offer reduced CO₂ capture costs.⁴⁻⁹ This regenerative cyclic process is based on the well-known capacity of CaO in reacting with gaseous CO₂ at high temperatures (600–750 °C) by forming solid CaCO₃.¹⁰ The controlled reactivity of CaO toward CO₂ was published by Barker in 1973. The carbonation reaction (eq 1), which is the one of interest, is highly exothermic, while the decarbonation (also called calcination) reaction (eq 1, backward step) is an endothermic process.¹¹⁻¹⁴

\[
\text{CaO}(s) + \text{CO}_2(g) \leftrightarrow \text{CaCO}_3(s) \quad \Delta H_{\text{r},298 K} = -178 \text{ kJ/mol} \tag{1}
\]

The concept of Ca-looping can be integrated in a variety of plants, with the most promising ones being the cement production plants. It also offers many other advantages, including the use of well-established fluidized-bed technology and recycling of spent sorbent.⁶,¹¹,¹⁵ Natural sorbents, such as limestone and dolomite, have been recently considered by several researchers as suitable candidates, because of their low price, availability, and reuse as feedstock for the cement industry,⁵,¹⁶ although they become less reactive upon cyclic operations, because of sintering, which occurs predominantly during the high-temperature calcination step.⁹,¹⁷,¹⁸ This usually leads to a decrease of particle surface area and reactivity falling to an asymptotic value of 0.08 g_{CO_2}/g_{sorbent} in the case of limestone.⁹,¹⁸ There are still questions about the long-term behavior of natural sorbents in such systems related to the sorbent activity loss with increasing number of reaction cycles,¹⁹ and there is substantial research and development being performed on this technology worldwide to answer questions about whether the performance of natural limestone...
sorbents can be improved, or whether it would be better to use synthetic ones. The use of synthetic Ca-based sorbents or a reactivation step can substantially reduce this decay in carbonation capacity, but the benefit of the very low cost of natural limestones may be lost. In that perspective, an efficient sorbent with (i) high adsorption capacity, (ii) high selectivity, (iii) high calcium oxide content allowing cyclic operation without losing carrying capacity, (iv) good mechanical resistance to attrition, and (v) being economically viable, still remains a challenge.

With the demand of a huge amount of solid CO\textsubscript{2} sorbents, the development of low-cost materials that can uptake CO\textsubscript{2} efficiently will undoubtedly enhance the competitiveness of adsorptive separation for CO\textsubscript{2} capture in flue gas applications.

Because of growing environmental concerns, important current research activities are focusing on the preparation of useful materials from the recovery of wastes.

Presently, large amounts of industrial byproduct solid wastes or residues are generated worldwide every year with serious consequences to the environment and humans. Large amounts of calcium-based industrial solid wastes containing Ca(OH)\textsubscript{2} and CaCO\textsubscript{3} are produced from the different chemical industries, such as carbide slag, alkaline paper mill lime mud, and red mud.

Carbide slag is a typical industrial waste, mainly composed of Ca(OH)\textsubscript{2} generated as a byproduct of the hydrolysis of calcium carbide (CaC\textsubscript{2}) during the industrial production of ethylene, which has recently been investigated to be used as a CaO-derived solid sorbent, or also for the preparation of a synthetic sorbent (from carbide slag, aluminum nitrate, and glycerol water solution) for CO\textsubscript{2} capture during calcination/carbonation cycles at high temperature in a thermogravimetric analyzer and also in a dual fixed-bed reactor. In 2014, Li et al. recently showed that carbide slag can be used for the simultaneous CO\textsubscript{2}/HCl removal in the adsorption/desorption cycles at an optimum CO\textsubscript{2}/HCl adsorption temperature of 700 °C and a desorption temperature in the range of 850–900 °C, and they concluded that the carbide slag with small particles should be chosen to achieve high CO\textsubscript{2} adsorption.

In 2012, Li et al. also investigated raw and treated lime mud (prewashed with distilled water and dried at 120 °C for 20 h), which is a calcium-based solid waste produced from the paper industry, for sequential SO\textsubscript{2}/CO\textsubscript{2} capture in the calcium looping process. The results obtained by these authors indicate that the treated lime mud appears to be a good SO\textsubscript{2}/CO\textsubscript{2} sorbent in the calcium looping process; however, compared with the natural limestone, the treated lime mud exhibited a lower carbonation conversion during the first five cycles with an initial carbonation conversion of 45%, but it showed a higher carbonation conversion after five cycles. In 2014, Li et al. also proposed a prolonged adsorption duration treatment of the raw and prewashed lime mud from the paper industry, to improve the CO\textsubscript{2} capture capacity in the multiple adsorption/desorption cycles. With this prolonged adsorption treatment, the area and volumes of pores 10–100 nm in diameter for CaO derived from both the raw and the prewashed lime mud increase, leading to an improvement of the cyclic rate of CO\textsubscript{2} adsorption, but the prewashed lime mud exhibits a higher cyclic rate of CO\textsubscript{2} adsorption than the raw lime mud.

The results that have been presented in the literature for the use of high-calcium-content alimentary wastes as raw materials to prepare CaO-based sorbents for CO\textsubscript{2} capture show that calcium-rich alimentary wastes can be used as solid CO\textsubscript{2} sorbents. However, in some cases, such as calcium waste that is composed of egg shells, shellfish shells, and cuttlefish bones, the observed initial carrying capacities (the first cycle) are very low and the decay profiles during multiple carbonation–calcination cycles showed that all the samples lose some of their carrying capacity as the number of cycles increases.

Worldwide, there has also been an increased interest in the recovery, recycling, and conservation of natural waste resources as key parameters for any sustainable development plants.

Wang et al. recently published a review on the advances in solid sorbents for CO\textsubscript{2} capture and the new development trends, where they referenced some works using CaO-based CO\textsubscript{2} sorbents from waste resources such as eggshells and mussel shell, shellfish, and cuttlefish bones, as well as paper industrial solid waste, but these authors do not reference or present any studies and, to date, there are no studies in the literature on the use of natural CaO-based waste resources such as natural waste marble powder (WMP) residues as possible inexpensive solid sorbents for Ca-looping cycle CO\textsubscript{2} capture.

Marble is a CaCO\textsubscript{3}-based rock and an important natural resource in Portugal, representing 5% of the world marble production. The high volume of marble production is accompanied by a considerable amount of waste marble powder (WMP) generated as a byproduct during the cutting and polishing procedures of the marble rock. The waste is in the range of ~20% of the total marble handled, and each marble producer plant generates a huge amount of WMP every year (250–400 tonnes), which negatively impacts the surrounding environment. Traditionally, the marble cutting plants are dumping the WMP in any nearby pit or vacant spaces, or disposing of it as soil conditioners or landfills, leading to serious environmental threats. In order to properly dispose of this large amount of WMP, the use of innovative techniques to recycle them is important.

Therefore, the main goal and innovative idea addressed in this paper consists of investigating if solid waste WMP from marble producer sources can be used as possible inexpensive and effective solid materials, to be used as precursors of CaO-based sorbents in Ca-looping cycle CO\textsubscript{2} post-combustion capture process. The main driving force for this work is the potential to reduce the cost of the Ca-looping cycle CO\textsubscript{2} capture process, as well as to minimize the adverse environmental impacts of the high volume of WMP generated in the marble producers.

The reactivity toward CO\textsubscript{2} uptake ability of several WMP sorbent samples obtained after sieving through different particle size fractions from the two as-received initial WMP\textsubscript{α} and WMP\textsubscript{β} samples provided by two different Portuguese marble producer sources, is studied using a laboratory-scale fixed-bed reactor system for the cyclic carbonation–calcination reactions, and their performance (initial carbonation capacity, stability/reactivity decay with the number of cycles) is compared with the performance of a reference sorbent obtained from commercial CaCO\textsubscript{3}, and with other natural and synthetic CaO-based sorbents, and other CaO-solid-based materials from industrial and natural wastes recovery, reported in the literature. The study includes the comparison of the results obtained for the samples with nondifferentiated particle sizes and the corresponding samples with different particle sizes ranges (same WMP source), and also the comparison of the two
different WMP sources with the same range of smaller particle sizes (63–125 μm).

2. EXPERIMENTAL SECTION

2.1. Preparation of the Sorbent Materials. Two natural WMP samples collected from two Portuguese marble producer plants in the region of Estremoz (Portugal) were used as precursors of CaO-based sorbents.

The as-received marble WMP samples were manually grinded in powder form and sieved through CISA sieves (sizes of 63, 125, 250, and 355 μm) and different particle size fractions were obtained. The denotations given to the WMP sorbent samples tested are presented in Table 1.

Table 1. Denotations of the Samples of WMP CaO-Based Sorbents Studied

<table>
<thead>
<tr>
<th>notation</th>
<th>remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>WMPα</td>
<td>nondifferentiated particle sizes</td>
</tr>
<tr>
<td>WMPα,63,125</td>
<td>particle size = 63–125 μm</td>
</tr>
<tr>
<td>WMPα,250,355</td>
<td>particle size = 250–355 μm</td>
</tr>
<tr>
<td>WMPβ</td>
<td>nondifferentiated particle sizes</td>
</tr>
<tr>
<td>WMPβ,63,125</td>
<td>particle size = 63–125 μm</td>
</tr>
</tbody>
</table>

The samples were oven-dried at 120 °C to ensure there was no initial moisture content.

The reference CaO sorbent was prepared by calcining commercial calcium carbonate (CaCO3) powder (Merck, 99.99%) at 800 °C for 3 h.

2.2. Characterization of the WMP Sorbent Materials. The composition of the fresh WMP samples on a mass basis was determined by chemical analysis.

The Brunauer–Emmett–Teller (BET) surface area (SBET) and the pore size distribution (PSD) of the fresh dried, calcined, and used (after 10 carbonation–calcination cycles) samples were assessed by N2 sorption, at 77 K, using a Micromeritics ASAP 2010 apparatus. Before measurement, the samples were outgassed under vacuum at 90 °C for 1 h and then at 350 °C for 4 h. The total pore volume (Vtotal) was calculated from the adsorbed volume of nitrogen for a relative pressure (P/P0) of 0.99. Surface areas were calculated by applying the BET equation, while PSD distribution was obtained by using the Barrett–Joyner–Halenda (BJH) method (desorption branch).

The morphology of the fresh and used samples was examined by scanning electron microscopy (SEM). Micrographs were acquired for samples covered with a thin Au–Pt film, using an FEI-SEM microscope (JEOL, Model 7001F).

Powder X-ray (PXRD) diffraction patterns were obtained using an X-ray diffractometer (Bruker, Model D8 Avance) with Cu Kα radiation operating at 40 kV and 40 mA, in order to identify the different crystalline phases present in the fresh and used samples.

Thermogravimetric (TGA) analysis of the fresh dried WMP sorbent samples were carried out on a thermal analysis system (SETARAM, Model TGA92), allowing the weight loss of each sample to be monitored with increasing temperature under inert atmosphere (nitrogen), until reaching a plateau of 850 °C.

The amount of CO2 released during calcination of the fresh dried WMP samples between 600 °C and 850 °C, was determined based on the sample weight loss during calcination, allowing the calculation of the initial CaO mass composition of each calcined sorbent sample.

2.3. CO2 Carbonation–Calcination Laboratory-Scale Fixed-Bed Reactor Tests. Reactivity testing with cyclic carbonation–calcination reactions was carried using an experimental laboratory-scale fixed-bed reactor system. The experimental system consists of a gas feeding system, a reactor system with temperature control, and a CO2 gas analyzer.

The reactor system includes an oven and a quartz reactor with an internal diameter of 4.5 cm and a length of 4.5 cm with a porous plate with a pressure drop of 1.7 mbar for a flow rate of 600 mL min–1 (P = 1 bar; T = 20 °C). Each WMP sample (10 g) was loaded into the reactor and prior to any CO2 carbonation–calcination cycle, in order to remove preadsorbed CO2 and H2O, each sample was first activated (to ensure the complete conversion of CaCO3 to CaO) by heating it from room temperature under a flow of pure N2 (850 mL/min) at a rate of 50 °C/min until achieving 800 °C and kept constant for 10 min. The sample then was cooled to 700 °C and the carbonation was conducted at a flow of 15% v/v CO2 (at a rate of 150 mL/min in N2 balance) for 8 min. After the carbonation, the CO2 flow was disconnected. The samples were heated to 800 °C under a flow of pure N2 (850 mL/min) and the temperature was kept constant at 800 °C for 8 min to complete the calcination in an atmosphere of N2 with the conversion of CaCO3 to CaO. Following the calcination process, the samples were cooled once more to 700 °C for the carbonation process.
of a new cycle. This carbonation—calcination cycle was repeated for the given number of cycles while continuously monitoring the CO2 concentration of the reactor outlet gas stream with a CO2 infrared gas monitor sensor (Guardian Plus 30%).

A mass balance was performed in order to evaluate the accuracy of the measurements and also to characterize the efficiency of the sorbent. The mass balance in the present study is written as the following expression:

$$m_{CO_2} = (m_{CO_2})_{hot\ capt} + (m_{CO_2})_{capt}$$

where $m_{CO_2}$ corresponds to the mass of CO2 fed to the reactor during the carbonation time; $(m_{CO_2})_{hot\ capt}$ is the mass of CO2 measured in the off-gas during carbonation (thus, the CO2 that did not react); and $(m_{CO_2})_{capt}$ represents the mass of CO2 measured in the off-gas during calcination corresponding to the mass of CO2 from the inlet stream that reacted with the CaO sample.

On the left-hand side of eq 2, the calculation of the amount of CO2 in the inlet stream is a simple straightforward calculation, multiplying the mass flow rate of CO2 by the duration of the carbonation step. On the right-hand side, the parameters of eq 2 are determined by calculating the area for carbonation and calcination stages (Figure 1). However, carbonation (region $S_1$ in Figure 1a) and calcination (region $S_3$ in Figure 1a) sections overlap at area $S'$ represented in Figure 1b.

When each carbonation step ends, the CO2 flow in the inlet feed is disconnected at 700 °C. If there was no CO2 release at the end of the carbonation period, the CO2 concentration would decrease in the same way as in the blank preliminary testing performed with the same atmosphere and temperatures but with no sorbent and no reaction, attending zero exit-gas CO2 concentration. The two curves, CO2 concentration from the fresh noncalcined WMP and WMP sorbent can be calculated based on the following equations:

$$F_{CO_2} = \int_{t_1}^{t_2} C_{CO_2}(t) Q_{N_2} \, dt$$

$$X_i \% = \frac{F_{W_{CaO}}}{m_{CaO}} \times 100$$

In eq 3, $F_{CO_2}$ (mol) is the amount of CO2 absorbed by the CaO-based sorbent at cycle $i$, $C_{CO_2}(t)$ is the CO2 fraction in the reactor outlet gas stream during calcination between time $t_1$ (s) and $t_2$ (s), $Q_{N_2}$ (L/s) is the volumetric flow rate of N2, during calcination, $V_m$ ($L/mol$) is the molar volume of CO2, whereas in eq 4, $X_i \%$ is the carbonation conversion of CaO in the sorbent at cycle $i$, $W_{CaO}$ (g/mol) is the molar weight of CaO, $m_{CaO}$ (g) is the sample mass after calcination determined from the results obtained in a preliminary thermogravimetric analysis (TGA) experiment, and $X_{CaO}$ is the CaO mass composition in the sorbent sample determined from the amount of CO2 released during calcination between 600 °C and 850 °C on the TGA preliminary analysis.

3. RESULTS AND DISCUSSION

3.1. Characterization of the WMP Sorbents. The presence of CaCO3 (calcite) as the main compound of the fresh noncalcined WMP and WMP sorbents dried at 120 °C, was confirmed by chemical elemental analysis (Table 2) and by XRD patterns (Figures 2a and 2c). In addition to Ca, C, and O, elemental analysis of both WMP sorbents (Table 2) reveals the presence of other elements, in trace amounts, including Si, Mg, Al, and Fe, with a trace element/Ca molar ratio of <0.05, with Si being the major trace element for both WMP sorbent samples. Under the CO2 absorption conditions used in the present work, auxiliary TGA experiments performed in this work showed that the oxide impurities had a negligibly low carbonation rate relative to CaO, and the amount of CO2 captured by these oxides impurities could be neglected. Table 2 also shows similar chemical compositions for both WMP fresh sorbents, although WMPα has a much higher content of Si and Al trace elements.

In agreement with the results obtained from chemical elemental analysis, the XRD patterns of the fresh WMPα and WMPβ sorbents dried at 120 °C revealed the presence of one main phase ascribed to CaCO3 (calcite) (see Figures 2a and 2c). Figures 2b and 2d also show similar XRD patterns for the WMPα and WMPβ sorbent samples after 10 carbonation—calcination cycles. As expected, it is clear that, after 10 carbonation—calcination cycles, CaO (lime) is the dominant phase present on both calcined samples of the used WMPα and WMPβ sorbents. In the case of fresh WMPβ sorbent,
The textural properties, BET surface area \( (S_{\text{BET}}) \), pore volume \( (V_p) \), and average pore diameter \( (d_p) \) of the WMP sorbent samples determined by nitrogen sorption measurements are presented in Table 3, whereas isotherms are shown in Figures 3 and 4 to facilitate the comparison of the different sorbent samples. Figure 5 shows the pore size distribution (PSD) from BJH desorption branch.

Table 3. Textural Properties of WMP Sorbent Samples Determined by Nitrogen Sorption Measurements

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>( S_{\text{BET}} ) (m(^2)/g)</th>
<th>( V_p ) (cm(^3)/g STP)</th>
<th>( d_p ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WMP(_a)</td>
<td>2.8</td>
<td>0.02</td>
<td>740</td>
</tr>
<tr>
<td>WMP(_a)-cal</td>
<td>6.1</td>
<td>0.03</td>
<td>1060</td>
</tr>
<tr>
<td>WMP(_a)-10 cycles</td>
<td>15.7</td>
<td>0.12</td>
<td>310</td>
</tr>
<tr>
<td>WMP(_a)-355</td>
<td>3.0</td>
<td>0.02</td>
<td>770</td>
</tr>
<tr>
<td>WMP(_a)-125-cal</td>
<td>13.6</td>
<td>0.04</td>
<td>800</td>
</tr>
<tr>
<td>WMP(_a)-125-10 cycles</td>
<td>10.0</td>
<td>0.07</td>
<td>180</td>
</tr>
<tr>
<td>WMP(_a)-355-355</td>
<td>5.9</td>
<td>0.02</td>
<td>1020</td>
</tr>
<tr>
<td>WMP(_a)-355-10 cycles</td>
<td>14.1</td>
<td>0.13</td>
<td>320</td>
</tr>
<tr>
<td>WMP(_b)</td>
<td>1.1</td>
<td>0.01</td>
<td>740</td>
</tr>
<tr>
<td>WMP(_b)-cal</td>
<td>10.9</td>
<td>0.05</td>
<td>530</td>
</tr>
<tr>
<td>WMP(_b)-3 cycles</td>
<td>20.2</td>
<td>0.08</td>
<td>130</td>
</tr>
<tr>
<td>WMP(_b)-10 cycles</td>
<td>35.4</td>
<td>0.20</td>
<td>270</td>
</tr>
<tr>
<td>WMP(_b)-125</td>
<td>1.0</td>
<td>0.01</td>
<td>780</td>
</tr>
<tr>
<td>WMP(_b)-125-cal</td>
<td>17.5</td>
<td>0.09</td>
<td>500</td>
</tr>
<tr>
<td>WMP(_b)-125-10 cycles</td>
<td>12.7</td>
<td>0.11</td>
<td>210</td>
</tr>
</tbody>
</table>

All the fresh WMP samples dried at 120 °C are nonporous (or macroporous) solid materials with similar pore volumes of <0.02 cm\(^3\)/g, and similar BET surface areas of < 3 m\(^2\)/g (Table 3). The low porosity of the CaO-based WMP fresh sorbents calcined under air was confirmed by nitrogen isotherms (Figure 4). In fact, all the calcined fresh WMP samples present a Type II curve characteristic of nonporous or macroporous solid materials, and, as expected, all the fresh calcined WMP samples (both with differentiated or nondifferentiated particle sizes) have a higher BET surface area and a higher porous volume than the fresh dried samples. This increase in WMPs surface area and pore volume during calcination is mainly due to the release of CO\(_2\) and other volatile compounds from the CaCO\(_3\)-based WMP sorbent precursors at high temperature (see Table 3, Figure 3).

On the other hand, the calcined WMP\(_a\), WMP\(_b\), and WMP\(_{a\text{-}355}\) have lower \( S_{\text{BET}} \) values than the calcined fresh samples presenting smaller grain sizes, namely, WMP\(_{a\text{-}125}\) and WMP\(_{b\text{-}125}\) (Table 3, Figure 3). In the case of sample WMP\(_{a\text{-}125}\), there is a higher increase in the \( S_{\text{BET}} \) and \( V_p \) values after calcination for the fresh sample, compared to the WMP\(_a\) and WMP\(_{a\text{-}355}\) samples, probably because of the smaller grain sizes of WMP\(_{a\text{-}125}\). Similar values of \( S_{\text{BET}} \) and \( V_p \) obtained for the calcined fresh samples WMP\(_a\) and WMP\(_{a\text{-}355}\) indicate that the nondifferentiated particle sizes WMP\(_a\) is mainly composed of particle sizes in the range of 250–355 μm (see Table 3 and Figure 3a).

Table 3 and Figure 3 also show an unusual feature, i.e., a significant increase of the BET surface area and of the pore volume after 10 carbonation–calcination cycles for the used sorbent samples with nondifferentiated particle sizes WMP\(_{a\text{-}10\text{cycles}}\) (increases of 157% in \( S_{\text{BET}} \) and 300% in \( V_p \) are observed) and WMP\(_{b\text{-}10\text{cycles}}\) (increases of 225% in \( S_{\text{BET}} \) and 300% in \( V_p \)), and for the sample with the higher range of particle sizes WMP\(_{a\text{-}250–355\text{-}10\text{cycles}}\) (increases of 139% in \( S_{\text{BET}} \) and 550% in \( V_p \)). This increase is also followed by an important decrease in the average pore diameter \( (d_p) \) (decreases of 71% for WMP\(_{a\text{-}10\text{cycles}}\), 69% for WMP\(_{b\text{-}10\text{cycles}}\), and 49% for WMP\(_{b\text{-}5\text{cycles}}\) are observed). The results obtained for the BET surface area for sorbent sample WMP\(_{a\text{-}3\text{cycles}}\) after 3 carbonation–calcination cycles (Table 3 and Figure 3b), clearly show that this unusual increase in \( S_{\text{BET}} \) and \( V_p \) is gradual with the increase of the number of cycles. These unexpected results obtained for the WMP sorbents have not yet been found in the literature for other natural limestones used without any pretreatment. Typical results found in the literature for nitrogen sorption analyses of natural limestone sorbents show that CO\(_2\) cycling of the original sorbent leads to a decreased surface area, which is usually explained by sintering and loss of pore surface area, because of shrinkage of the smaller pores, usually accompanied by growth of the macropores. 35 These trends are typical of solid-state sintering in an intermediate stage, as described by sintering theory 39 in which vacancies (or voids) generated by temperature- and ion-sensitive lattice defects direct void volume from smaller to larger pores, whereas the mass flow moves in the opposite direction, from larger pores to smaller ones.

The results presented in Figure 4 show the corresponding nitrogen sorption isotherms obtained for the different samples of fresh air-calcined and used WMP sorbents after the carbonation–calcination cycles. The particular shape of these
isotherms can give a possible explanation of the unexpected results discussed above. The isotherms for the used WMP\textsubscript{\alpha}10 cycles, WMP\textsubscript{\beta}10 cycles, and WMP\textsubscript{\alpha}250−355−10 cycles samples correspond to type IV with a type H1 hysteresis, both of which are typical of mesoporous solid materials. The pore size distributions curves (PSDs from BJH desorption branch) from Figure 3. Comparison of the textural properties of the different samples of (a) WMP\textsubscript{\alpha} sorbents and (b) WMP\textsubscript{\beta} sorbents.

Figure 3. Comparison of the textural properties of the different samples of (a) WMP\textsubscript{\alpha} sorbents and (b) WMP\textsubscript{\beta} sorbents.

Figure 4. N\textsubscript{2} sorption isotherms for the different samples of fresh calcined and used sorbents: (a) WMP\textsubscript{\alpha} and (b) WMP\textsubscript{\beta}.

Figure 4. N\textsubscript{2} sorption isotherms for the different samples of fresh calcined and used sorbents: (a) WMP\textsubscript{\alpha} and (b) WMP\textsubscript{\beta}.

Figure 5. Pore size distributions (PSDs from BJH desorption branch) for the different samples of fresh calcined and used sorbents: (a) WMP\textsubscript{\alpha} and (b) WMP\textsubscript{\beta}.

Figure 5. Pore size distributions (PSDs from BJH desorption branch) for the different samples of fresh calcined and used sorbents: (a) WMP\textsubscript{\alpha} and (b) WMP\textsubscript{\beta}.
50 Å to ca. 1000 Å for the different samples of fresh calcined and used sorbents presented in Figure 5, show that the WMP fresh calcined sorbents have low pore volume but very large mesopores (maxima centered at ca. 950 Å for WMPα samples and ca. 550 Å for WMPβ samples). The PSD curves (Figure 5) obtained for the used WMP sorbents after the 10 carbonation–calcination cycles show a higher pore volume than that observed for the original fresh calcined samples, with only one peak for pore widths below 500 Å, corresponding to a peak maximum of ca. 290 Å for WMPα–10 cycles and WMPβ–10 cycles, 180 Å for WMPα–10 cycles, 270 Å for WMPβ–10 cycles, and ca. 210 Å for WMPβ–10 cycles. Indeed, during the carbonation–calcination cycling process of the WMP samples, there is an increase in the pore volume Vp (not including macropores), mainly because of the formation of mesopores with smaller average pore diameters (dp) than in the initial fresh calcined sorbents.

This increase in mesopore volume with smaller pores can explain the observed unexpected increase of the BET surface area with the increasing number of carbonation–calcination cycles for these WMP sorbent samples. Several researchers [3,38,40] have noted a bimodal pore size distribution of calcined particles that is created upon calcination of the sorbents. The smaller pores presumably arise because of CO2 being driven off during calcination of the newly formed calcium carbonate, whereas larger pores are not only present in the initial limestone, but also formed due to internal sintering that occurs during calcination at high temperature, leading to severe aggregation of calcium crystals and grains, causing pore structure changes with the aggregation of micropores and mesopores, shifting vacancies from smaller to larger macro pores, driven by minimization of the surface energy. [39] In 2005, Alvarez and Abanades studied the pore-size and pore-shape effects of CaO particles on the recarbonation performance of natural limestones for the capture of CO2, and they observed that the initial PSD split into two different populations of pores: a decreasing one of smaller pores, always peaking at ~900 Å, and the other population of pores continuously shifting to bigger sizes, because of the sintering of the unreacted CaO. [30] The loss of small pores in natural limestone sorbents was also observed by several researchers that propose a mechanism where the large pores continuously increase in size with the number of cycles as a consequence of the internal sintering that occurs during calcination at high temperature. This possible continuous increase in size of the large pores with pore widths bigger than 500 Å initially present in the fresh calcined samples, with the carbonation–calcination cycles was not observed in our study, because of the limitations of the technique (i.e., the PSD curves for the WMP sorbents shown in Figure 5 were obtained from the BJH desorption branch with an experimental pore width detection limit of ~1000 Å). Therefore, it is not possible to conclude if the large pores have shifted to larger macropore sizes. Although other researchers [7] have also observed BJH pore size distributions with two peaks, one of them in the micropore size range, in the case of the present study with WMP sorbents, the fresh calcined samples did not show microporosity. However, it is expected that, during calcination of the newly formed calcium carbonate, small pores presumably arise in WMP particles, because of CO2 being driven off during calcination. As can be seen for the used sample WMPβ–3 cycles after 3 carbonation–calcination cycles, the corresponding PSD curve (Figure 5) clearly shows a peak maximum at ~130 Å, smaller than the average pore width observed for WMPβ used after 10 carbonation–calcination cycles (Table 3, Figure 5). Therefore, this means that, for these WMP sorbent samples, during the first cycles, there might also

Figure 6. SEM images (scale bar = 1 μm) of sorbent WMPα: (a) fresh dried, (b) fresh calcined, (c) used after 10 cycles, and (d) used after 20 cycles.
occur a mechanism of aggregation of micropores to mesopores during calcination, in agreement with the observed increase of the average pore width from 130 Å for WMP<sub>β-3</sub> cycles after 3 cycles to ca. 270 Å for WMP<sub>β-10</sub> cycles after 10 carbonation–calcination cycles.

On the other hand, in the case of samples with the smaller particle sizes (63–125 μm), WMP<sub>α-63–125-10</sub> cycles and WMP<sub>β-63–125-10</sub> cycles although there is an increase of the pore volume after 10 cycles, Table 3 and Figures 3a and 3b show a decrease in the BET surface area, which is a behavior usually reported in the literature for other used natural or synthetic CaO-based sorbents, because of the sintering of the small sorbent particles that may occur during high-temperature calcination, causing the sorbent grain growth and blockage of the pore entrances.

The morphology of fresh sorbent samples dried at 120 °C, fresh calcined, and used after 3, 10, or 20 carbonation–calcination cycles was analyzed by SEM microscopy (Figures 6–8).

The micrographs in Figures 6a, 7a, and 7d show that the different fresh WMP<sub>α</sub> samples, with differentiated or non-differentiated particle sizes, are composed of layered agglomerates, as shown in the SEM images (Figures 7 and 8).
erates of particles with a large particle size distribution. The air-calcined fresh samples are composed of aggregates of coral-like structures or networks of small particles with different sizes but smaller than those observed for the fresh dried samples (Figures 6b, 7b, and 7e), in agreement with the higher \( S_{\text{BET}} \) and \( V_p \) values obtained for those samples (see Table 3).

The SEM images in Figures 6c, 6d, 7c, 7f, 8a, and 8b, corresponding to different used WMP sorbent samples, reveal dismantled aggregates of sintered and smaller particles with visible fissures and cracks, which are more pronounced in the case of sample WMP\( \alpha \) used after 20 carbonation−calcination cycles (Figure 6d). These fissures or cracks may be responsible for the formation of mesopores, in agreement with the above-discussed increase obtained for the BET surface area and of the pore volume after the carbonation−calcination cycles (Figures 6c, 6d, 7c, 7f, 8a, and 8b). In fact, the extent of the cracked structure seems to increase with the number of cycles.

The structures observed for the WMP samples are remarkably different from the structure obtained for the reference commercial CaCO\(_3\) fresh sorbent precursor consisting of nonporous compact aggregates of large cubic particles (average particle diameter = 30 \( \mu \)m), which also present cracks after the 10 carbonation−calcination cycles (Figure 9). The corresponding \( S_{\text{BET}} \) of the air-calcined fresh commercial CaCO\(_3\) sorbent is 8 m\(^2\)/g,\(^21\) which is within the range of the values obtained for the WMP air-calcined sorbents (Table 3), and \( V_p = 0.04 \text{ cm}^3/\text{g} \),\(^21\) which is similar to the \( V_p \) values presented in Table 3 for the WMP air-calcined sorbents.

### 3.2. Reactivity of the WMP Sorbents

The CO\(_2\) sorption capacity of the different WMP sorbent samples was studied during multiple carbonation−calcination cycles. The reactivity study of the WMP samples showed that WMP waste can be successfully used as CaO-based sorbents for CO\(_2\) capture in the looping cycle process. All the different WMP sample sorbents tested in the fixed-bed reactor have similar initial CO\(_2\) sorption capacity and deactivation profile evolution with the number of cycles (see Figures 10a and 10b). This means that, for the WMP sorbents tested, sorbent particle sizes in the range of <355 \( \mu \)m do not represent an important parameter for determining the WMP reactivity profiles.

As reported in the literature for natural limestones or other CaO-based sorbents,\(^{14,21,22,30,41}\) similar evolution profiles for the carbonation−calcination cycles have been obtained for all the WMP sorbents tested, showing that the exothermic carbonation reaction is characterized by two stages: an initial fast surface reaction controlled by the reaction kinetics and a slower reaction controlled by the diffusion of CO\(_2\) into the bulk CaCO\(_3\) product.

Figure 10a shows the temporal evolution of the CaO carbonation conversion for 10 carbonation−calcination cycles...
of the tested CaO-based WMP sorbents and of the reference CaO sorbent from commercial CaCO₃, while Figure 10b shows the temporal evolution of the carbonation conversion for 20 cycles for sorbent WMPₐ with no differentialed particle sizes.

Very high initial carbonation (first cycle) conversions (between 89.7% and 93.3%) can be observed for the WMP samples tested, which is a very interesting result, since these initial carbonation conversions are higher than the initial carbonation conversion of 78.6% obtained in this study for the commercial CaCO₃ used as reference sorbent (Figure 10a), and also higher than the initial carbonation conversion (first cycle) of other natural and synthetic CaO-based sorbents reported in the literature, such as Kelly Rock, La Blanca, and Katowice natural limestones (between 78% and 86%), Graymont natural limestone (ca. 77%); Strassburg natural limestone (ca. 77%); Havelock natural limestone (ca. 80%); Havelock natural limestone (ca. 80%); Jining (JN) natural limestone (ca. 80%); Kelly Rock and Cadomin natural limestones (between 71% and 74%); synthetic CaO-based sorbents hydrated by steam/superheating (between 37% to 79%); Havelock natural limestone (ca. 68%) and synthetic PCC-precipitated CaCO₃ (ca. 73%); Maoming (MM) limestone (ca. 80%); and synthetic CaO-based sorbents prepared by biotemplated synthesis (between 47% and 84%). Also, when compared with other CaO-solid-based materials from industrial and natural wastes or residues recovery, the natural WMP sorbents tested in the present study show a higher initial carbonation conversion (first cycle) than the initial carbonation conversion reported in the literature for the following calcium wastes: carbide slag industrial waste (between 80% and 85%); raw lime mud waste (ca. 20%) and prewashed lime mud waste (ca. 45%); mussel shell (ca. 54%); scallop shell (ca. 67%); and Mactra veneriformis shell (ca. 87%); and oyster shells (ca. 64%).

As reported in the literature for natural limestones or other CaO-based sorbents after synthesis/modification of sorbents (doped and supported sorbents, and reactivated through steam/water hydration), the observed decay profiles in the temporal evolution of the carbonation conversion of the WMP sorbents during the cycling CO₂ sorption process (Figures 10a and 10b) also reveal a decrease in the CO₂ carrying capacity with an increasing number of carbonation–calcination cycles. However, it is useful to notice that the WMP sorbents tested exhibit better cyclic stability with a lower sorbent deactivation with the number of cycles than the reference CaO sorbent from commercial CaCO₃; in the first 10 cycles, the WMP sample sorbents show a reactivity decrease between 36% and 44%, while the CaO-based sorbent from commercial CaCO₃ shows a higher reactivity decrease of 50% (Figure 10a).

Sample WMPₐ was also tested for 20 carbonation–calcination cycles, and the results presented in Figure 10b show that the rate of the sorbent deactivation decreases with the number of cycles, with the carbonation conversion reaching a constant level of conversion of 43.3%.

Several authors consider that this typical deactivation may be caused by the sintering of CaO sorbent particles that may occur during high-temperature calcination, causing the sorbent deactivation due to grain growth and pore shingkage, shifting vacancies from smaller to larger macropores, or pore blockage, with the corresponding reduction in surface area; or by competing reactions. However, the unexpected result highlighted by the present study in the case of WMP sorbents with nondifferentiated particle sizes (WMPₐ and WMPₐβ) and with the higher range of particle sizes (WMPp₂ to WMPpₐ) is that, along with a significant increase of the BET surface area and mesopore volume with smaller mean pore diameter sizes as the number of carbonation–calcination cycles increases (Table 3, Figures 3 and 5), there is a decrease of the CaO carbonation conversion (Figure 10). So, this result indicates an apparent contradiction, because, although there is an increase of the BET surface area with the number of cycles, the available quantity of surface CaO for the carbonation reaction decreases with the number of cycles for WMP sorbents with nondifferentiated particle sizes (WMPpₐ and WMPpₐβ) and with the higher range of particle sizes (WMPp₂ to WMPpₐ). Considering the earlier claims by other researchers that the morphologic characteristics, such as porosity and surface area of the sorbents, are the most important factors in the control of the CaO conversion in limestones, the results obtained in this work show that, in the case of WMP CaO-based sorbents, the average pore sizes between 100 and 300 Å or the corresponding pore mouth sizes, are not large enough to prevent the pore plugging (and further blocking) by CaCO₃ freshly produced during carbonation. Although the increase in the surface area of the WMP samples may provide a large number of chemisorption sites inside the smaller pores for interaction with CO₂, once CO₂ reacts with CaO at a pore mouth during the fast stage of the carbonation step, the CaCO₃, which has a density that is significantly lower than that of CaO, can block the pores in the case of narrow bottleneck pore mouths, and turn the CaO sites inside the pores unavailable for the progress of the reaction with CO₂ during the remaining carbonation time in each cycle. Therefore, the effect of the increase of the surface area and of the pore volume due to the formation of mesopores smaller than the initial macropores, on the sorbents carbonation conversion with the number of cycles, must have been severely hampered by its limited pore mouth size. This deactivation process proposed for explaining the decrease in the carbonation conversion by pore blockage or closure of small pore mouths during the fast initial carbonation of the WMP particles, was also indicated by Lu et al. in 2006 as the main factor in the decaying carbonation performance in multiple carbonation–calcination cycles of a synthetic CaO sorbent prepared from calcium acetate precursor and doped with SiO₂. These authors also considered a mechanism of blockage and collapse of the pore structure, rather than the sorbent sintering effects usually found in the literature.

This pore blockage deactivation mechanism, relative to the number of carbonation–calcination cycles, does not contradict the observed increase of the mesopore volume after 10 cycles for WMP sorbents in the present study, because when the pore blocking carbonate is calcined, the pores reopen and their free CaO internal volume and surface become available again for CO₂ adsorption.

Other more-complex pore distributions and textural effects may appear under some conditions, but the discussion of these is beyond the objective of this work.

The differences observed in the morphological and textural properties of the two types of WMP α and β sorbents (WMPₐ and WMPpₐ) with or without differentiated ranges of particle sizes (Table 3) did not result in very different reactivity profiles for the CO₂ carrying capacity since all the WMP sorbents samples tested in this study in the fixed-bed reactor, have similar initial CO₂ sorption capacities between carbonation...
The higher initial carbonation (first cycle) conversions and the better cyclic stability with a lower sorbent deactivation with the number of cycles for the different tested WMP sorbents, when compared to the reference CaO obtained from calcination of commercial CaCO₃, cannot not only be explained by the differences on the morphologic characteristics such as porous volume and surface area of the sorbents particles, but the extent of carbonation and the BET surface areas of the sorbents particles, which were claimed to be responsible for the reference commercial CaO. However, the better cyclic stability with a lower sorbent deactivation with the number of cycles of the different tested WMP sorbents can possibly be due to the increase of mesopores volume along the carbonation–calcination cycles (see Figure 4). This formation of mesoporosity does not happen in the case of the reference CaO sorbent from commercial CaCO₃ sorbent precursor, and it has not been reported in the literature for the cases of other natural CaO-based sorbents. The presence of other elements in trace amounts including Si, Mg, Al, and Fe, in the chemical composition of the WMP sorbents may have an important role in the formation of this mesoporosity during the carbonation–calcination cycles. In the cases of limestone-derived and oyster-shell-derived CaO-based sorbents, it has been reported that the extent of carbonation and the deactivation with the number of cycles can be promoted by the existence of inactive impurities, which were claimed to be capable of stabilizing the CaO framework from sintering. Based on the analytical results obtained in 2010 by Ma and Teng, these authors proposed that the impurities contained in oyster shells would form a transition zone, which surrounds the CaO crystal grains and hinders crystal growth with sintering. A wide transition zone surrounding CaO crystal grains would lead to gradual lattice expansion in CO₂ fixation. With a narrow transition zone, an abrupt lattice expansion would occur, causing lattice dislocations and, thus, a decay in CO₂ absorption capacity. However, the influence of impurity structure on the carbonation performance of CaO-based sorbents is still under investigation.

Further research is needed to improve the understanding of the relationship between the WMP sorbents reactivity and deactivation upon looping cycle CO₂ capture, and the structural and morphological characteristics, as well as the influence of the inactive impurities present in the WMP sorbents.

4. CONCLUSIONS

This experimental study demonstrates the ability of waste marble powders (WMP) to be used as promising CaO-based sorbents with high carrying capacity efficiency and good stability upon CaO-looping cycle CO₂ post-combustion capture technology. Multiple carbonation–calcination cycles over the WMP-derived CaO-based sorbents are characterized by a gradual decay of sorption capacity.

The new and unexpected result highlighted by this work in the case of WMP sorbents with nondifferentiated particle sizes (WMP₁ and WMP₂) and with the higher range of particle sizes (WMP₃ (250–355 µm)) is that, along with a significant increase of the BET surface area and of the mesopore volume with smaller mean pore diameter sizes observed with the increasing number of carbonation–calcination cycles, there is a decrease of the CaO carbonation conversion. This apparent contradiction can be explained by a deactivation mechanism of small pore mouths blocking, in the case of narrow bottleneck pore mouths, by the formation of CaCO₃, with density significantly lower than that of CaO during the fast stage of the CaO carbonation step at a pore entrance, which makes the CaO sites inside the pores unavailable for the progress of the reaction with CO₂ during the remaining cycle carbonation time.

The higher initial carbonation (first cycle) conversions obtained for the different tested WMP sorbents, when compared with the reference CaO obtained from calcined commercial CaCO₃, cannot not only be explained by the differences on the morphologic characteristics, such as pore volume and surface area of the sorbents particles, but the observed better cyclic stability and the lower sorbent deactivation with the number of cycles of the different tested WMP sorbents can be due to the significant increase of the mesopore volume with smaller mean pore diameter sizes observed along the carbonation–calcination cycles. This effect has not been reported in the literature for other natural CaO-based sorbents. The presence of other elements in trace amounts, including Si, Mg, Al, and Fe, in the chemical composition of the WMP sorbents may have an important role in the formation of this mesoporosity during the carbonation–calcination cycles.

The temporal evolution of the CaO carbonation conversion obtained for the calcined WMP sorbent samples tested with different ranges of particle sizes (differentiated or non-differentiated) does not show significant differences between them, which also demonstrates that the strong differences in sorbents structural and textural characteristics such as the particle sizes, the BET surface area, and the pore volume, are not the only parameters that mainly influence the CO₂ uptake ability performance of the natural WMP sorbents. Further research is needed to improve the understanding of the relationship between the WMP sorbents reactivity and deactivation upon looping cycle CO₂ capture, and the changes in structural and morphological characteristics in multiple carbonation–calcination cycles, and also the influence of the inactive impurities present in the WMP sorbents.

The innovative results presented in this study show that natural Portuguese waste marble powders (WMP) have the potential to be an economically attractive option to be used as inexpensive CaO-based sorbents for CO₂ post-combustion capture, thus contributing to reduce the cost of the Ca-looping cycle CO₂ capture process, as well as minimizing the adverse environmental impacts of the high volume of WMP generated in the marble producers.

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Notes
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