CO₂ capture performance of Ca-Mg acetates at realistic Calcium

Looping conditions

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Abstract

The Calcium Looping (CaL) process, based on the cyclic carbonation/calcination of CaO, has emerged in the last years as a potentially low cost technique for CO₂ capture at reduced energy penalty. In the present work, natural limestone and dolomite have been pretreated with diluted acetic acid to obtain Ca and Ca-Mg mixed acetates, whose CO₂ capture performance has been tested at CaL conditions that necessarily imply sorbent regeneration under high CO₂ partial pressure. The CaL multicycle capture performance of these sorbents has been compared with that of CaO directly derived from limestone and dolomite calcination. Results show that acetic acid pretreatment of limestone does not lead to an improvement of its capture capacity, although it allows for a higher calcination efficiency to regenerate CaO at reduced temperatures (~900°C) as compared to natural limestone (>~930°C).

On the other hand, if a recarbonation stage is introduced before calcination to reactivate the sorbent, a significantly higher residual capture capacity is obtained for the Ca-Mg mixed acetate derived from dolomite as compared to either natural dolomite or limestone. The main reason for this behavior is the enhancement of carbonation in the solid-state diffusion controlled phase. It is argued that the presence of inert MgO grains in the mixed acetate with reduced segregation notably promotes solid state diffusion of ions across the porous structure created after recarbonation.

Keywords: CO₂ capture; Calcium Looping; modified limestone; modified dolomite; thermogravimetry

1. Introduction

The Calcium-Looping (CaL) process is being widely investigated in the last years as a potential solution to capture CO₂ from energy intensive industries such as coal fired power plants [1-2]. The process is based on the reversible carbonation/calcination of CaO solids in two interconnected fluidized bed reactors using low cost (~10\$/ton), widely available and non-toxic natural limestone (close to 100% CaCO₃) as CaO precursor [3-5]. CO₂ from the flue gas stream is captured in a carbonator reactor by chemical reaction of CaO with CO₂ after which the carbonated solids are circulated into a second fluidized bed reactor (calciner) where CaO is regenerated by calcination, which releases a concentrated CO₂ stream to be compressed, transported and stored or employed in other uses [3, 6-7]. Conditions of the CaL process for post-combustion capture involve short residence times and gas velocities of a few m/s in both reactors. The concentration of CO₂ in the carbonator is around 15% vol. as typical of flue gas, and the optimum working temperature is around 650°C. In the calciner, CaO regeneration and calcination of the fresh limestone makeup must take place under CO₂ at high concentration (70-90% vol.), which requires operation at temperatures above 930°C. Calcination at high temperatures under high CO₂ partial pressure is a drawback for integrating the CaL process into industrial plants. On one hand, it poses an energy penalty for the technology [8-9]. On the other, it causes a marked aggregation and sintering of the CaO nascent grains during the CaCO₃/CaO transformation, which leads to a drastic decrease of the CaO surface area available for quick carbonation in a subsequent cycle [10-11]. As demonstrated in previous studies [12], carbonation of CaO particles takes place through two different phases. The first phase is controlled by reaction kinetics until a CaCO₃ layer is built upon the surface of the particle, after which carbonation becomes ruled by the solid-state counter-current diffusion of ions across

100 this product layer. The short residence time employed for carbonation in the CaL
101 process is thought to constrain the CO₂ capture efficiency in practice to the fast reaction
102 phase at the surface of the particles [13]. In order to mitigate the drastic loss of CaO
103 activity, it has been proposed to introduce a recarbonation stage between the
104 carbonation and calcination stages [14-15]. The operation temperature of the
105 recarbonator would be around 800°C, and CO₂ concentration should be high in order to
106 accelerate carbonation in this intermediate stage (~90% vol.). Calcination of the
107 recarbonated solids would yield a CaO skeleton with enhanced porosity and therefore
108 higher carbonation activity in short residence times.

109 The trade between cost of the Ca-based sorbent and its CO₂ capture capacity is a critical
110 issue for scaling up this technology to an industrial level [16]. Natural limestone is the
111 main candidate to be used at large-scale due to its wide availability, non-toxicity and
112 low price [3-4, 17-19]. Yet, the fast deactivation rate of limestone derived CaO (lime)
113 has sparked research on synthetic materials, such as CaO-based sorbents modified with
114 organic acids to produce calcium acetate, calcium propionate or calcium citrate among
115 others [16, 20-24]. Li et al. reported promising results from CO₂ capture tests using
116 calcium magnesium acetate [25]. The sorbent derived from dolomite treated with acetic
117 acid showed indeed a superior multicycle conversion behavior as compared with CaO
118 directly derived from dolomite calcination (dolime) under the same experimental
119 conditions. The role of MgO on improving the conversion behavior of Ca-Mg synthetic
120 sorbents for CO₂ capture has been widely investigated in previous works. Thus, it has
121 been observed that calcium acetate and carbide slags sintering is mitigated by the
122 addition of small amounts of MgO [26-28]. Other authors have employed commercial
123 calcium magnesium acetates with diverse calcium to magnesium molar ratios and found
124 that CaO conversion was enhanced as the magnesium content was increased [29]. Wet

mixing combustion synthesis has been also employed to prepare sorbents with diverse amounts of MgO [30]. Coprecipitation is another technique that has been used to prepare synthetic Ca-rich dolomites, with high and stable CaO conversion [31]. However, calcination conditions play a crucial role on the behavior of Ca-based sorbents when subjected to CaL cycles [32-33]. To the best of our knowledge, CaO sorbents derived from calcium and calcium magnesium acetates have been mostly tested under mild calcination conditions involving low CO₂ partial pressure environments. Yet, realistic CaL conditions for CO₂ capture necessarily involve calcination under high CO₂ partial pressure.

This work is focused on investigating the multicycle CO₂ capture behavior of CaO derived from calcium acetate and calcium magnesium acetate at CaL conditions implying sorbent regeneration under high CO₂ partial pressure as expected in practice.

2. Materials and methods.

The materials employed in this work were natural limestone received from Segura S.L. (Matagallar quarry, Pedrera, Spain) of high purity (99.6%wt CaCO₃) and natural dolomite from Bueres quarry (Asturias, Spain). The predominant phase (94.4% wt.) of dolomite is CaMg(CO₃)₂, with the rest being CaCO₃ (~5%) plus impurities (<1%).

Acetic acid of high purity (99.9%) from VWR Chemicals (CAS: 64-19-7) was used to prepare the acetates.

As a first step, limestone and dolomite were precalcined in a muffle furnace at 900°C for 2 hours in air to obtain the corresponding oxides. CaO derived from limestone and CaO·MgO from dolomite calcination were treated with diluted acetic acid (50% vol. in aqueous solution), at a ratio of 8.1 g per 140 mL for CaO and 8.5 g per 120 mL for

CaO·MgO. Then, the mixture was magnetically stirred at room temperature for 24 hours and dried at 120°C.

The instrument used to perform the carbonation/calcination and carbonation/recarbonation/calcination multicycle tests was a thermogravimetric analyzer (TGA) Q5000IR from TA Instruments. The instrument is equipped with an infrared halogen lamp furnace. Four lamps are placed symmetrically with respect to a SiC enclosure, which allows for fast heating/cooling transitions (300°C/min). In CO₂ capture applications, the solids are rapidly circulated between the reactors; therefore, the transition between stages in TGA tests must be fast in order to mimic realistic conditions. Otherwise, a slow transition from carbonation to calcination would lead to a prolonged recarbonation of the sorbent that would critically affect its multicycle behavior. The TGA instrument is also equipped with a high sensitivity balance (<0.1 µg), characterized by a minimum baseline dynamic drift (<10 µg). A thermocouple positioned close to the sample underneath it registers the temperature during the cycles. The conditions employed in this work consist of a precalcination stage carried out by increasing the temperature (300°C/min) up to 900°C under 30% air/70% CO₂ vol/vol. atmosphere. Carbonation/calcination (carb/cal) tests are initiated by quickly decreasing the temperature for carbonation at 650°C under typical flue gas conditions (85% air/15% CO₂ vol/vol.). Then, the sample is calcined by increasing again the temperature up to 900°C under 30% air/70% CO₂ vol/vol. As will be seen, an advantage of the use of Ca and Ca-Mg acetates is that calcination is efficient in short residence times under this reduced temperature as compared to limestone, which requires calcination temperatures typically above 930°C to achieve full decarbonation in short residence times [1]. Residence times of 5 minutes for both calcination and carbonation stages have been used as typical reference times at practical conditions. In the experiments in

which a recarbonation stage was introduced after carbonation, it was carried out for 3 minutes at 800°C under 90% CO₂/10% air (vol/vol). The mass employed for testing the multicycle behavior of the different materials was ~5.5 mg with the objective of avoiding undesired effects caused by poor mass transfer phenomena and gas diffusion resistance through the samples [34].

Scanning Electron Microscopy (SEM) micrographs were taken using an ultra-high resolution HITACHI S5200 instrument. X-Ray diffractograms were acquired in the 2θ range from 5° to 90° using a Panalytical X'Pert Pro diffractometer working at 45 kV and 40 mA with CuKα radiation, and equipped with an X'Celerator detector and a graphite diffracted beam monochromator.

3. Results and discussion.

3.1. Acetic acid pretreatment of natural limestone and dolomite.

Figure 1 shows the X-ray diffraction patterns registered for limestone and dolomite after being treated with the diluted acetic acid solution.

As may be seen in Figure 1a, the main Bragg reflection peaks observed for modified limestone correspond to partially hydrated Ca acetate. A minor peak indicates the existence of a quite small amount of Ca-Mg acetate produced by the presence of MgO impurities in the raw limestone [35-36]. On the other hand, the reflection peaks observed for modified dolomite (Figure 1b) correspond to Ca-Mg acetate, with a secondary, albeit non negligible, phase of Ca acetate [36], which will be referred to hereafter as Ca-Mg mixed acetate.

Figure 1. X-ray diffraction patterns of limestone (a) and dolomite (b) used in our experiments after pretreatment with diluted acetic acid.

Thermal decomposition of these Ca and Ca-Mg mixed acetates was studied by thermogravimetry. Figure 2 shows the thermograms obtained by heating the samples from room temperature to 950°C at 10°C/min in an air flow of 50 cm³/min. As may be seen, Ca acetate (Ca(CH₃COO)₂) decomposes mainly in three steps. In the first one (about 5% mass loss), dehydration takes place at temperatures between 134°C and 201°C. The second mass loss (around 35% of the total mass) occurs from 360°C to 417°C, whereby the decomposition of Ca(CH₃COO)₂ in CaCO₃ and acetone ((CH₃)₂CO) occurs via the reaction:

Finally, the last mass loss (26%) takes place in the range from 620°C to 728°C due to the calcination of CaCO_3 to yield CaO :

Figure 2b shows the thermal decomposition of the Ca-Mg mixed acetate obtained from natural dolomite. The relatively important presence of Ca acetate yields some deviations over the mass loss expected for pure Ca-Mg acetate. Thus, the mass loss in the first stage (2%) corresponds to dehydration at temperatures from 138°C to 194°C. Afterwards, the decomposition of the mixture of acetates in the corresponding carbonates and acetone takes place between 326°C and 427°C (40% mass loss):

In previous works, it has been proposed that decomposition of Ca-Mg acetate yields the corresponding amounts of Ca and Mg carbonates as separate byproducts [37]. In our case however, the co-existence of Ca acetate has to be taken into account in the stoichiometry of the process (reaction 3). Between 430°C and 460°C decomposition of MgCO_3 , which has lower thermal stability than CaCO_3 , takes place:

In the last decomposition phase, whereby about 10% of the total mass is lost, CaCO_3 decomposes in the temperature range from 611°C to 686°C. A 33% of the initial mass

remains after full decomposition is achieved, which corresponds to a mixture of CaO and MgO (Figure 2b).

Figure 2. Temperature evolution of mass (% of initial mass) and its time derivative (right axis) during thermal decomposition of (a) Ca acetate and (b) Ca-Mg mixed acetate obtained from limestone and dolomite pretreated with diluted acetic acid, respectively (heating rate 10°C min⁻¹ under air).

3.2. Scanning electron microscopy analysis (SEM)

The microstructure of the Ca acetate and the Ca-Mg mixed acetate derived from limestone and dolomite, respectively, before and after the multicycle tests was analyzed by SEM. Micrographs of both acetates are shown in Figure 3. As can be seen, the samples exhibit the characteristic rod-shape grains of these acetates [38-41]. Note also how these rods are thinner for the Ca-Mg mixed acetate.

Figure 3. SEM micrographs of (a) limestone and (b) dolomite modified with acetic acid.

SEM micrographs obtained for the acetates after being subjected to multicycle calcination/carbonation tests (as detailed in section 3.3) are shown in Figure 4. Figure 5 presents SEM micrographs of the sorbents after the cycles in which a recarbonation stage was introduced between carbonation and calcination. The cycled Ca acetate typically presents fissures, large pores and marked sintering of the CaO grains. On the other hand, the cycled sample of the mixed Ca-Mg acetate shows a higher porosity. CaO grains in this sample are of typically smaller size compared to those observed for the cycled Ca acetate and can be clearly distinguishable from the MgO grains. The latter remain inert to carbonation under the CaL conditions used in our tests and would presumably help mitigating aggregation and sintering of the CaO grains as inferred from previous works for natural dolomite [17, 42]. It is thus foreseeable that the capture capacity of the Ca-Mg mixed acetate is improved as compared to Ca acetate.

Figure 4. SEM micrographs of (a, b) Ca acetate and (c, d) Ca-Mg mixed acetate after 20 cycles consisting of 5 minutes carbonation at 650°C (15% CO₂/85% air vol/vol) and 5 minutes calcination at 900°C (70% CO₂/30% air vol/vol).

Figure 5. SEM micrographs of (a) Ca acetate and (b) Ca-Mg mixed acetate samples after 20 carbonation/recarbonation/calcination cycles. Carbonation at 650°C (15% CO₂/85% air vol/vol) for 5 minutes, recarbonation at 800°C (90% CO₂/10% air vol/vol) for 3 minutes, and calcination at 900°C (70% CO₂/30% air vol/vol) for 5 minutes.

3.3. CO₂ capture capacity

Figure 6 shows multicycle calcination/carbonation thermograms obtained for Ca acetate and the Ca-Mg mixed acetate. As can be seen, complete decomposition of the CaO precursors is achieved from the 1st calcination at 900°C under a 70% CO₂/30% air vol/vol atmosphere. This is a substantially lower temperature than the minimum temperature needed to achieve full calcination of natural limestone in short residence times (over 930°C) [17]. Thus, as a first important result it may be inferred that the use of acetates would allow operating the calciner at a reduced temperature compared to natural limestone, which would allow for a reduction of the energy penalty [1, 8-9].

Figure 6. Time evolution of temperature and mass % during calcination/carbonation cycles measured by thermogravimetric tests on samples of Ca acetate (a) and Ca-Mg mixed acetate (b). Carbonation at 650°C (15% CO₂/85% air vol/vol) for 5 minutes and calcination at 900°C (70% CO₂/30% air vol/vol) for 5 min. Precalcination at 900°C (70% CO₂/30% air vol/vol) for 5 min.

This behavior suggests that the CaCO_3 formed in the second decomposition step of calcium acetate and calcium magnesium acetate is less crystalline than natural limestone, which favors decarbonation at reduced temperatures as seen in previous works for limestone and dolomite samples mechanically milled to reduce crystallinity [43]. With the objective of confirming this hypothesis, calcium acetate was decomposed at 500°C to yield CaCO_3 and the XRD pattern was registered to compare it with that of natural limestone measured in the same conditions. In Figure 7 the main XRD reflections for both samples are shown. It is clear that, although the peak widths are similar, the peak intensities for CaCO_3 obtained from calcium acetate are smaller than for limestone. This indicates that calcium acetate derived CaCO_3 has a significantly lower crystallinity than limestone, which favors decarbonation.

Figure 7. X-ray diffraction patterns obtained for natural limestone and CaCO_3 derived from Ca acetate decomposed at 500°C .

The parameter used to compare the multicycle performance of the sorbents analyzed in our work is their capture capacity, which takes into account the presence of compounds inert to carbonation such as MgO in the sorbents derived from dolomite. The capture capacity is defined as the mass gained during carbonation (mass of CO₂ captured in this stage) divided by the mass of sorbent before carbonation was started including inert species. As can be observed in Figure 6, the mass gained during the carbonation stages for the acetate derived from dolomite (Figure 6b) is remarkably higher than for the acetate derived from limestone (Figure 6a), which indicates a superior capture performance of this sorbent as will be discussed in more detail below.

Multicycle capture capacity data for the Ca acetate are shown in Figure 8. Results are compared with data obtained for CaO directly derived from natural limestone calcination (in this case the minimum calcination temperature to achieve full decomposition from the first cycle was 950°C). As can be seen in Figure 8a, the capture capacities measured for the Ca acetate are clearly below those obtained for natural limestone. The introduction of a recarbonation stage (Figure 8b) when testing the Ca acetate leads to slightly higher values of the capture capacity in the first cycles, albeit also clearly below those corresponding to natural limestone. Therefore, it may be concluded that the acetic acid pretreatment on limestone does not lead to an improvement of its multicycle capture performance under realistic CaL conditions, which is a consequence of the marked sintering of CaO derived from calcium acetate, as observed in Figures 4a, 4b and 5a. Nevertheless, a reduction of the calcination temperature can be achieved, which would serve to mitigate the energy penalty in the integration of the CaL process into a power plant to be carefully assessed by heat integration analysis [44].

Figure 8. a): Capture capacity versus carbonation/calcination cycle number for CaO samples derived from Ca acetate and natural limestone. Precalcination at 900°C (70% CO₂/30% air vol/vol) for 5 minutes, carbonation (carb) at 650°C (15% CO₂/85% air vol/vol) for 5 minutes, and calcination (cal) at 900°C (70% CO₂/30% air vol/vol) for 5 minutes (in the case of limestone calcinations are carried out at 950°C). b) Data from tests in which a recarbonation (rec) stage was introduced (90% CO₂/10% air vol/vol for 3 min at 800°C) between the carbonation and calcination stages. The solids lines are the best fit curves of Equation (5) to experimental data (values of the residual capture capacity obtained from these best fits are shown in the inset).

As for Ca acetate, calcination of the Ca-Mg mixed acetate was fully achieved at 900°C in short residence times (Figure 6b), which was thereby used also as calcination temperature for sorbent regeneration. Multicycle capture capacity data obtained for the Ca-Mg mixed acetate are plotted in Figure 9, where results on the capture capacity of the sorbent derived from natural dolomite calcination are also shown for comparison. As may be observed, the capture capacity curve of the Ca-Mg mixed acetate is slightly below that of natural dolomite (Figure 9a). On the other hand, the introduction of the recarbonation stage is in this case seems to mitigate substantially the deactivation of

CaO derived from the mixed acetate (Figure 9b). Thus, the values of capture capacity for this sorbent are higher from the 7th cycle as compared to those obtained for the sorbent directly derived from natural dolomite calcination when a recarbonation stage is introduced.

Figure 9. Capture capacity data versus carbonation/calcination cycle number for sorbents derived from the Ca-Mg mixed acetate and natural dolomite. Carbonation at 650°C (15% CO₂/85% air vol/vol) for 5 minutes and calcination at 900°C (70% CO₂/30% air vol/vol) for 5 minutes. A recarbonation at 800°C (90% CO₂/10% air vol/vol) for 3 minutes is introduced in b). The solids lines are the best fit curves of Equation (5) to experimental data (values of the residual capture capacity obtained from these best fits are shown in the inset).

Multicycle capture capacity data obtained from the TGA tests were fitted using the semi-empirical equation [11, 45-46]:

$$CC_N = CC_r + \frac{CC_1}{k(N-1) + (1 - CC_r/CC_1)^{-1}}; \quad (N = 1, 2 \dots) \quad (5)$$

where N is the cycle number, CC_1 is the capture capacity at the first cycle, CC_r is the residual capture capacity, towards which the capture capacity converges asymptotically after a very large number of cycles, and k is the deactivation rate constant. As may be seen, in Figures 8 and 9, Eq. (5) fits quite well to experimental data, which allows us to infer a value of the residual capture capacity for the different sorbents tested (Table 1 and insets of Figures 8-9). From these values, it can be concluded that the treatment with acetic acid may lead to an improvement of the multicycle CO_2 capture performance but only for natural dolomite and under carbonation/recarbonation/calcination cycles. In this case a relatively high residual capture capacity is obtained ($CC_r = 0.168$).

Table 1. Residual capture capacity (CC_r) values for CaO derived from calcination of Ca acetate, natural limestone, Ca-Mg mixed acetate and natural dolomite.

	Carb. (min)	Recarb. (min)	Calc. (min)	CC_r
Ca acetate	5	--	5	0.054
	5	3	5	0.045
Limestone	5	--	5	0.055
	5	3	5	0.107
Ca-Mg acetate	5	--	5	0.087
	5	3	5	0.168
Dolomite	5	--	5	0.112
	5	3	5	0.088

3.4. Relative role of fast-reaction and solid-state diffusion controlled carbonation phases

Figure 10 shows the time evolution of the capture capacity during the 20th carbonation for the sorbents analyzed in this work. Carbonation of CaO proceeds through two differentiated phases. Under carbonation at 650°C, a fast reaction-controlled (FR) stage occurs first until a carbonate layer of about 30-50 nm thickness is built on the surface of the particles [47-48]. The FR phase is followed afterwards by a relatively slower phase, which is governed by the counter-current solid-state diffusion (SD) of O²⁻ and CO₃²⁻ ions across the product layer [49]. Figure 10 shows also that a great part of the overall capture capacity is due to carbonation in the SD phase when sorbent regeneration is carried out under high CO₂ partial pressure according to practical conditions, which contrasts with most of previous observations from tests in which calcination was performed under low CO₂ partial pressure [50].

Figure 10. Time evolution of CO₂ capture capacity during the 20th cycle for (a) Ca acetate and limestone and (b) Ca-Mg mixed acetate and dolomite. Calcination at 900°C (70% CO₂/30% air vol/vol) for 5 minutes, carbonation at 650°C (15% CO₂/85% air vol/vol) for 5 minutes and recarbonation at 800°C (90% CO₂/10% air vol/vol) for 3 minutes. “I” indicates the fast reaction-controlled phase and “II” the slow solid-state diffusion-controlled phase. In the case of limestone calcination was carried out at 950°C to achieve full decarbonation from the 1st cycle.

Let us analyse in further detail the relative contribution of the FR and SD carbonation phases to the overall CaO conversion along the carbonation/calcination cycles and how it is affected by the introduction of a recarbonation stage. CaO conversion is defined as the ratio of CaO mass converted to CaCO₃ at the end of the carbonation stage to the mass of CaO before carbonation. In the case of limestone derived sorbents, conversion is simply calculated by multiplying the capture capacity by the factor $W_{\text{CaO}}/W_{\text{CO}_2}$, where W_{CaO} and W_{CO_2} are the molecular weights of CaO and CO₂ respectively. For the dolomite derived sorbents, CaO conversion is calculated by multiplying the capture capacity by $(1+W_{\text{MgO}}/W_{\text{CaO}})(W_{\text{CaO}}/W_{\text{CO}_2})$, where W_{MgO} is the molecular weight of MgO. The separated contributions of the FR and SD phases to the overall CaO conversion, as derived from the experimental thermograms, are shown in Figure 11 as a function of the cycle number for the sorbents derived from the acetates. CaO conversion data in the FR and SD phases are plotted in Figure 12 for the sorbents directly derived from limestone (Figures 12a and 12b) and dolomite calcination (Figures 12c and 12d).

In general, it may be seen that CaO conversion in the FR phase is relatively small as compared to conversion in the SD phase. As reported in previous works [10-11], calcination under high CO₂ partial pressure yields a highly sintered CaO structure with a quite reduced surface area available for fast reaction controlled carbonation, which severely hampers carbonation in this initial phase. On the other hand, the diffusion controlled stage is relatively promoted. The relative importance of SD carbonation is a relevant point to assess the influence of solids residence time in the carbonator on the capture efficiency when the CaL process is integrated into a coal fired power plant as demonstrated in [44]. It must be reminded that most carbonator modelling studies use data derived from thermogravimetric analyses in which the sorbents are regenerated by calcination under unrealistic low CO₂ partial pressure, which leads to negligible

carbonation in the SD phase during the first cycles in clear contrast with our observations [14].

Figure 11. CaO conversion in the fast reaction controlled phase (a and c) and in the solid-state diffusion controlled phase (b and d) versus the cycle number for the sorbents derived from Ca acetate and Ca-Mg mixed acetate as indicated. Calcination at 900°C (70% CO₂/30% air vol/vol) for 5 minutes, carbonation at 650°C (15% CO₂/85% air vol/vol) for 5 minutes and, when introduced, recarbonation at 800°C (90% CO₂/10% air vol/vol) for 3 minutes.

As regards the effect of recarbonation, Figures 11a-b show that, for the Ca acetate, the slight gain of CaO conversion is mainly due to the promotion of carbonation in the FR phase. In this case, recarbonation would enhance, although just moderately, the porosity of the regenerated CaO structure. The low values of CaO conversion in the FR phase for this sorbent are consistent with the marked sintering observed for CaO derived from calcium acetate in Figures 4a, 4b and 5a. The reactivation effect of recarbonation is however more evident in the case of natural limestone (Figures 12a-12b). In this case,

recarbonation yields a noticeable effect on conversion both in the FR and in the SD phases.

Figure 12. CaO conversion in the fast reaction controlled phase (a and c) and in the solid-state diffusion controlled phase (b and d) versus de cycle number for the sorbents derived from limestone and dolomite. Calcination at 900°C (70% CO₂/30% air vol/vol) for 5 minutes, carbonation at 650°C (15% CO₂/85% air vol/vol) for 5 minutes and, when introduced, recarbonation at 800°C (90% CO₂/10% air vol/vol) for 3 minutes as indicated. Limestone calcination was carried out at 950°C to achieve full decarbonation from the 1st cycle.

The enhancement of CaO conversion in the SD phase is more marked for the sorbents derived from dolomite (Figures 11c-11d and 12c-12d) as compared to limestone. In these cases, the presence of MgO inert grains in the solid structure would favor ion diffusion as may be inferred from the work of Anderson [51-52], who measured by isotope exchange diffusion coefficients two orders of magnitude larger in dolomite than the values in calcite. Note also that the recarbonation stage causes for dolomite an

increase of CaO conversion in the SD phase, which is marked for the Ca-Mg mixed acetate (Figure 11d). Moreover, deactivation in the FR phase is notably mitigated for this sorbent by the introduction of a recarbonation stage (Figure 11c).

Figure 13. Time evolution of CaO conversion during the 5 minutes of carbonation, 3 minutes recarbonation and 5 minutes calcination at the 10th cycle for (a) Ca acetate and the Ca-Mg mixed acetate and (b) Limestone and dolomite. Carbonation at 650°C (15% CO₂/85% air vol/vol), recarbonation at 800°C (90% CO₂/10% air vol/vol) and calcination at 900°C (70% CO₂/30% air vol/vol). Limestone calcination was carried out at 950°C to achieve full decarbonation from the 1st cycle. A schematic representation of carbonate layer growth is also shown in a).

Figure 13a shows the time evolution of CaO conversion during the 5 minutes carbonation, 3 minutes recarbonation and 5 minutes calcination stages at the 10th cycle for the sorbents derived from Ca acetate and the Ca-Mg mixed acetate. A schematic representation of the changes in the CaO product layer morphology is also shown as was inferred elsewhere by combining TGA and atomic force microscopy (AFM) using natural limestone [53-54]. According to this study, the CaCO₃ layer on the CaO surface would grow in the form of islands of height depending on surface diffusion. The raise of temperature at the beginning of the recarbonation stage leads to a sudden increase of surface diffusion, which allows the development of higher CaCO₃ islands while their density decreases. This leaves additional free CaO surface available for fast reaction controlled carbonation under high CO₂ partial pressure, and thereby leads to a significant growth of the CaCO₃ product layer. Thus, when the sorbent is regenerated by calcination after recarbonation, the thick carbonate layer would yield a CaO structure with relatively higher porosity and therefore enhanced surface area. This is the fundamental mechanism by which recarbonation is thought to promote the activity of the sorbent in the subsequent cycle. As seen in Figure 13, our results indicate that recarbonation is enhanced for the dolomite derived sorbents, which supports the idea that promoted carbonation in this stage is ruled by surface diffusion that would be favored by the presence of MgO inert domains. This is specially marked in the case of the Ca-Mg mixed acetate (Figure 13a), which suggests that the treatment with acetic acid would mitigate segregation of the MgO grains. This would explain also why deactivation of the Ca-Mg acetate derived sorbent is reduced as obtained from the multicycle capture capacity data (Figure 9b). In agreement with this argument, Figure 14 shows SEM micrographs of Ca-Mg mixed acetate and dolomite samples after being

subjected to carbonation/recarbonation/calcination cycles in which segregation of MgO and CaO grains is more apparent in the case of dolomite.

Figure 14. SEM pictures of Ca-Mg mixed acetate (a,b) and dolomite samples (c,d) after being subjected to 20 carbonation/recarbonation/calcination cycles. Carbonation at 650°C (15% CO₂/85% air vol/vol), recarbonation at 800°C (90% CO₂/10% air vol/vol) and calcination at 900°C (70% CO₂/30% air vol/vol).

4. Conclusions

In this work, the multicycle CO₂ capture performance of CaO derived from Ca and Ca-Mg mixed acetates obtained from acetic acid treatment of limestone and dolomite, respectively, has been studied at realistic Ca-Looping conditions. These necessarily involve calcination under high CO₂ partial pressure and fast transitions between carbonation and calcination stages.

Acetic acid treatment of limestone produces almost pure Ca acetate, with a minor amount of Ca-Mg acetate. On the other hand, acetic acid treatment of dolomite leads to a Ca-Mg mixed acetate consisting of a mixture of Ca-Mg acetate and Ca acetate. Acetic acid pretreatment of limestone allows for a higher calcination efficiency at reduced temperatures (900°C) as compared to natural limestone (>930°C) due to the relatively low crystallinity of the CaCO₃ derived from Ca acetate decomposition as compared to limestone. On the other hand, acetic acid pretreatment of limestone and dolomite does not lead to an improvement of their capture capacity under carbonation/calcination cycles, which is against previous results mostly obtained under CaL conditions involving unrealistically low CO₂ partial pressure in the calcination stage for sorbent regeneration. Yet, the results obtained also demonstrate that a significantly high residual capture capacity ($CC_r = 0.168$) is obtained for the Ca-Mg mixed acetate if a recarbonation stage is introduced as compared to natural dolomite ($CC_r = 0.088$). The main reason for this behavior is the enhancement of carbonation in the solid-state diffusion controlled phase, which confers a relevant role to the solids residence time in the carbonator on the CO₂ capture efficiency. Moreover, the progressive segregation of the MgO and CaO grains with the number of cycles is reduced in the case of the Ca-Mg mixed acetate as compared with dolomite, which helps mitigating sorbent deactivation.

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