***Calcium-Looping performance of mechanically modified $Al_2O_3$-CaO composites for energy storage and $CO_2$ capture***

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**Highlights:**

* $Al_2O_3$/limestone composites were prepared by ball milling with $Al_2O_3$ contents in the range between 5 and 20%wt

* The composites were subjected to calcination-carbonation cycles at conditions for $CO_2$ capture and energy storage

* Diverse types of calcium aluminate were formed as depending on the Calcium Looping conditions.

* High Al-content leads to deactivation mainly by the formation of $Ca_3Al_2O_6$ at $CO_2$ capture conditions

* At energy storage conditions, the residual effective conversion of the composites is twice that of limestone

**Abstract**:

This work reports the Calcium-Looping (CaL) multicycle performance under energy storage and $CO_2$ capture conditions of different Al-composites prepared by milling mixtures of nanoalumina and natural limestone powders. The micro- and nanostructure of the composites has been analyzed by X-ray diffraction, scanning electron microscopy and high-resolution transmission electron microscopy as affected by the type of CaL conditions employed, either for energy storage in Concentrated Solar Power (CSP) plants or for post-combustion $CO_2$ capture. Two types of calcium aluminates are formed under these diverse CaL conditions. A calcium aluminate with ratio Ca/Al < 1 ($Ca_4Al_6O_{13}$) is formed under CaL-CSP conditions, which helps stabilize the CaO microstructure and mitigate pore-plugging. On the other hand, a crystalline phase $Ca_3Al_2O_6$ is formed (Ca/Al > 1) under CaL-$CO_2$ capture conditions presumably due to the higher calcination temperature, which withdraws from the sorbent a relatively high amount of active Ca. Moreover, the addition of nano-alumina, and the consequent generation of calcium aluminates, affects in diverse ways the microstructure and morphology of the CaO particles as depending on the CaL application, which critically modifies the performance of the composites.

**Keywords**: Calcium Looping; Energy Storage; $CO_2$ capture; Concentrated Solar Power; Al-Ca composites

## 1. Introduction

The Calcium-Looping (CaL) process is at the basis of a 2nd generation $CO_2$ capture technology for removing $CO_2$ from post-combustion gases already demonstrated at large pilot scale (1-2 MWth) [1-5]. The process relies upon the reversible carbonation/calcination reaction of CaO

$$CaO_{(s)} + CO_{2\,(g)} \rightleftarrows CaCO_{3\,(s)}; \quad \Delta H_r^0 = -178 \text{ kJ/mol} \tag{1}$$

Carbonation takes place at temperatures around ~ 650 ºC in a fluidized bed reactor where the post-combustion flue gas carries a $CO_2$ concentration close to 15 vol% at atmospheric pressure. After carbonation, $CaCO_3$ particles are circulated into a second reactor (calciner) where calcination, under necessarily high $CO_2$ concentration and high temperature (~ 930-950ºC), regenerates the CaO particles [6, 7]. Once CaO particles are regenerated, they are recirculated into the carbonator for a subsequent new cycle. The $CO_2$ extracted from the calciner at high concentration can be thus compressed and stored or employed in other uses. This process is schematized in Figure 1a.

In the last years, the CaL process has acquired a renewed interest for Thermochemical Energy Storage (TCES) in Concentrated Solar Power (CSP) plants [8-11]. The $CaO/CaCO_3$ system offers a high energy storage density (about 3.26 $GJ/m^3$) which would allow electricity generation in CSP plants on demand overcoming the issues derived from the variable nature of direct solar irradiation [12, 13]. A detailed CaL-CSP energy integration scheme has been recently proposed by Chacartegui et al. [13]. Basically, the integrated system consists of a solar calciner, a carbonator, a $CO_2$ compression-storage system, two tanks for CaO and $CaCO_3$ storage and a Brayton-based power unit (Figure 1b) [13, 14]. Thus, the endothermic calcination reaction takes place when direct solar irradiation is available, which serves to store the excess heat as chemical energy, whereas the exothermic carbonation reaction is carried out at night or during limited solar activity, which releases heat to carried by the $CO_2$ in excess to the power block. The use of Helium gas in the calciner in a closed cycle helps reduce the calcination temperature in short residence times to about 700 ºC [15] due to the enhancement of the thermal conductivity and $CO_2$ diffusivity in He [16, 17]. The $He/CO_2$ mixture could be separated by selective membranes [18], allowing the storage and recirculation of the gases individually in both closed cycles.

The low price, wide availability and non-toxicity of natural Ca-based materials such as limestone, makes the CaL process very interesting for large-scale applications such as $CO_2$ capture and energy storage [19-23]. However, most of natural Ca-based materials exhibit a progressive deactivation as the number of carbonation/calcination cycles is increased, which is particularly marked at $CO_2$ capture conditions [6, 24, 25]. Thus, cost-effective treatments are being investigated to enhance the CaO multicycle stability such as thermal activation [26-29], hydration [29-31] and mechanical activation or milling [32-34]. An alternative strategy consists of the synthesis of composites through the controlled addition of inert materials with high Tamman temperature to stabilize the CaO structure [20, 21, 35]. Thus, the performance of Al-containing sorbents has been widely investigated at diverse CaL conditions [35-39]. Florin et al. [40] employed a coprecipitation method by bubbling $CO_2$ through an aqueous solution containing $Ca(OH)_2$ and $Al(NO_3)_3$ for the synthesis of Ca-based materials with different

contents of mayenite ($Ca_{12}Al_{14}O_{33}$) after calcination at 800 ºC. These authors found that the capture capacity of the composites increased as the binder aluminate content was increased. However, a proportion of $Ca_{12}Al_{14}O_{33}$ higher than 15 wt% yielded a decrease of the $CO_2$ capture capacity and hampered the mechanical stability of the composite. By means of a sol-gel method, Broda et al. [35, 37] synthesized gels with $Ca^{2+}/Al^{3+}$ molar ratios from 90/10 to 50/50, using aluminum isopropoxide and different Ca sources. After calcination at 800 °C for 2 hours a small amount of $Ca_{12}Al_{14}O_{33}$ was also formed. The results obtained from $CO_2$ capture multicycle tests indicated that the composite with higher activity had a Ca/Al molar ratio of 90/10. Recently, Sun et al. [33] analyzed the effect of the addition of gibbsite ($Al(OH)_3$, 5-40%) to natural limestone after milling using a planetary ball mill. They concluded that, despite the formation of $Ca_3Al_2O_6$ binder, the addition of Al did not yield clear benefits. However, grinding limestone did enhanced the $CO_2$ capture performance.

In recent years, the use of Ca/Al composites has been analyzed for thermochemical energy storage in CSP plants based either on the $CaO/Ca(OH)_2$ system [22] or $CaO/CaCO_3$ [41] for the storage of medium and high temperature heat, respectively. Sakellariou et al. [41] have analyzed the calcination/carbonation behavior of Ca/Al composites prepared from calcium and aluminum nitrates with different Ca/Al molar ratios (95/5, 80/20 and 52/48) following the modified Pechini route and calcining at 900 ºC for 2h under air atmosphere. They showed that the most effective compound (80/20 Ca/Al) exhibited a high surface area and a significant amount of $Ca_3Al_2O_6$ binder. However, an excessive formation of calcium aluminate caused a premature deactivation as was the case of the composite with the molar ratio of 52/48. In the same line, Obermeier et al. [42] synthesized different Al-composites (Ca/Al molar ratios of 95/5, 90/10, 80/20 and 75/25) from Ca-citrate and Al-nitrate, and analyzed their multicycle performance under CaL-CSP conditions introducing of a steam hydration stage at different temperatures. The results indicated that neither the temperature increase nor the presence of water vapor had a significant effect on the CaO performance.

Notwithstanding the different methodologies employed to synthesize Al-modified CaO sorbents, a simpler and cost effective method for producing large amounts of sorbent is needed. Just physical mixing and milling of natural limestone and Al-based compounds is a cost-effective technique poorly investigated for $CO_2$ capture [33] and, to our knowledge, unexplored yet for energy storage. The present work analyzes and compares for the first time the CaL multicycle performance under energy storage and $CO_2$ capture conditions of different composites prepared by milling powdered nanoalumina and limestone at different proportions. The research includes the analysis of the micro- and nanostructure of the composites by X-ray diffraction, scanning electron microscopy and high resolution transmission electron microscopy. As will be seen, two distinct types of calcium aluminate are formed as depending on the type of CaL conditions used which, in addition to microstructural effects, helps explain the diverse behaviors exhibited by the alumina composites as depending on the type of CaL conditions.

## 2. Materials and Methods

A high-purity limestone was employed in the present work from Taljedi quarry (Sevilla, Spain) (99.4% wt $CaCO_3$, with a small proportion of impurities such as 0.09% wt $Al_2O_3$, 0.09%

wt $Fe_2O_3$, 0.02%wt $K_2O$, 0.17% wt MgO, 0.17% wt $SiO_2$, 0.02% wt $P_2O_5$ and 0.02% wt $SO_3$). After sieving, the fraction above 160 μm was selected for the study.

The aluminum oxide nanopowder (Al content > 99.8%, supplied by Strem Chemicals) used as additive in this work is a quasi-amorphous alumina formed by the transition aluminas χ-$Al_2O_3$ (PDF card 13-0373) and γ-$Al_2O_3$ (PDF card 10-0425) (Fig. 2a). The alumina particles are mainly hexagonal platelets (Fig. 2b) of size between 0.3 and 5 μm, peaking at 1.65 μm (Fig. 2c). Surface area and granulometric data measured for the nanoalumina powder employed are collected in Table 1.

Mixtures of different nanoalumina content (5, 10 and 20 wt%) and limestone were prepared. In order to obtain homogeneous blends, the samples were milled at 1500 rpm during 90 s in an EMAX mill (Retsch) using stainless steel jars with 50 balls (10 mm diameter), a sample mass to balls mass fraction 1/20 and a 10 g sample. The as-synthetized alumina composites were named as **5wt $Al_2O_3$**, **10wt $Al_2O_3$** and **20wt $Al_2O_3$**. The $CaCO_3$ crystallite size was decreased to a minimum value (around 20 nm) for a grinding time of 90 s that remained the same for longer grinding periods.

Multicycle CaL tests were performed using a TA instrument Q5000IR thermogravimetric analyzer, which is provided with a high sensitive balance (< 0.1 μm) and a furnace heated by IR halogen lamps. IR heating allows high heating and cooling rates (up to 300 ºC/min) as well as stable isotherms. Fast heating/cooling rates are necessary to mimic realistic conditions since the material is circulated between reactors at different temperatures. All samples were tested under the following energy storage (CaL-CSP) and $CO_2$ capture (CaL-$CO_2$) conditions. The CaL-CSP experiments were started with a precalcination stage from room temperature to the calcination temperature (725 ºC) at 300 ºC/min under He atmosphere, and the isotherm was maintained during 5 min. Then, the carbonation step was initiated under pure $CO_2$, increasing the temperature (at 300 ºC/min) up to 850ºC, which was kept fixed for 5 min. Carbonation was followed by the calcination step under He through a quick temperature reduction (at 300 ºC/min) down to 725ºC, which was held for 5 min. An intermediate step was introduced after calcination by quickly decreasing the temperature to 300 ºC, which was kept fixed for 2 min under He. This cooling stage was intended to replicate the extraction of sensible heat of the solids after calcination and before storage as would be the case in the practical application [13]. After this cooling stage a new cycle was started for a total of 20 carbonation/calcination cycles. These conditions were selected according to the CaL-CSP integration scheme proposed by Chacartegui et al. [13] and were used also in previous works [15, 23, 43]. Multicycle CaL-$CO_2$ capture experiments were started by a calcination step from room temperature to 900 ºC (at 300 ºC/min, held for 5 min) under high $CO_2$ concentration (70% $CO_2$/ 30% air vol/vol) at atmospheric pressure. Precalcination was followed by a carbonation stage by quickly decreasing the temperature to 650 ºC at 300 ºC/min, which was held for 5 min under 15% $CO_2$/ 85% air vol/vol. A total of 20 carbonation/calcination cycles were also run. In all runs, a small mass (10 mg) was used for avoiding undesired effects related to $CO_2$ diffusion resistance across the bulk.

Particle size distributions (PSDs) were measured by laser diffraction analysis using a Mastersizer 2000 equipment (Malvern). For this purpose, the samples were previously dispersed in 2-propanol and sonicated for 30 s to loosen particle aggregates.

XRD powder measurements were carried out using a MiniFlex600 (Rigaku) with Ni filtered CuKα radiation (λ = 1.5406 Å) at 40 kV/15 mA for a scan range 2θ=5–90° and a scan speed of 3°/min. Crystallite size was estimated using the PDXL2 Rigaku data analysis software.

Nitrogen adsorption-desorption isotherms were measured at 77 K (-196 ºC) by employing a ASAP2420 (Micromeritics) instrument. Prior to the analysis, the samples were degassed at 350 ºC for 7 h. Total surface areas ($S_{BET}$) were determined using the BET equation [44]. Total pore volumes (Vsp) were calculated from the amount of $N_2$ adsorbed at a $P/P_0$ value of 0.99.

SEM micrographs of previously gold-sputtered samples were acquired using a Hitachi S4800 FEG microscope. HRTEM micrographs and high-angle annular dark-field scanning transmission electron micrographs (HAADF-STEM) were registered using a Talos F200S FEG microscope (FEI). For this purpose the powder samples were deposited on copper grids.

**Table 1**: $CaCO_3$ crystallite size (L, estimated using the main reflection peak (104) 2θ = 29.5º), PSD and porosimetry data for nanoalumina, milled limestone/alumina mixtures.

| | L (nm) | PSDs data (μm) | | | $S_{BET}$ ($m^2/g$) | $V_p$ ($cm^3/g$) |
|---|---|---|---|---|---|---|
| | | Dv(10)[a] | Dv(50)[b] | Dv(90)[c] | | |
| **$Al_2O_3$** | Amorphous | 0.9 | 1.7 | 2.9 | 271 | 0.24 |
| **Milled samples** | | | | | | |
| **0wt $Al_2O_3$** | 20 | 1.0 | 6.2 | 72 | 5 | 0.017 |
| **5wt $Al_2O_3$** | 23 | 0.9 | 4.0 | 46 | 16 | 0.027 |
| **10wt $Al_2O_3$** | 19 | 1.0 | 7.4 | 56 | 23 | 0.038 |
| **20wt $Al_2O_3$** | 20 | 1.0 | 6.6 | 52 | 39 | 0.050 |

a Particle size limit below which 10% of the particles are found

b Mass Median Diameter (MMD).

c Particle size limit below which 90% of the particles are found

## 3. Results and Discussion

Figure 3 shows the PSDs and representative SEM micrographs of the different composites prepared. As seen above (Table 1), the specific surface area and pore volume are progressively increased as the $Al_2O_3$ content is increased (Table 1). However, Figure 3 shows that particle morphology and size distribution are rather independent of the $Al_2O_3$ content. A bimodal distribution is observed in Fig. 3a, peaking at 1.6 and 18 μm. Additionally, a small proportion of larger aggregates, ranging from 200 to 800 μm, is observed. These agglomerates

could be generated by incomplete grinding or by cold welding of particles as reported in ball milling studies [45, 46].

### 3.1) *Calcium Looping (CaL)* Multicycle Activity

The effective conversion $X_{ef\ N}$ was the parameter utilized to evaluate the samples performances when subjected to multicycle CaL tests. $X_{ef\ N}$ is defined as the ratio of the CaO mass converted in the carbonation stage of each N-cycle to the total sample mass before carbonation

$$X_{ef\ N} = \frac{m_{Carb\ N} - m_N}{m_N} \cdot \frac{W_{CaO}}{W_{CO2}} \quad (2)$$

where $m_N$ and $m_{Carb\ N}$ are the sample masses before and after carbonation at the Nth-cycle and $W_{CaO}$ , $W_{CO2}$ are the molar masses of CaO and $CO_2$, respectively. The effective conversion takes into account the presence of inert compounds in the composites by using the total sample mass $X_{ef\ N}$. Consequently, the specific energy released in the carbonation stage per unit mass would be given by $X_{ef}$ times ($\Delta Hr^0/W_{CaO}$) (kJ/g), where $\Delta Hr^0$ is the reaction enthalpy (-178 kJ $mol^{-1}$).

Data on the effective conversion measured for the different composites under energy storage and $CO_2$ capture conditions are shown in Figure 4. These data can be well fitted by the semi-empirical equation [47-49]:

$$X_{ef\ N} = X_{ef\ r} + \frac{X_1}{k(N-1) + \left(1 - {}^{X_r}/_{X_1}\right)^{-1}} \quad (3)$$

where $N$ is the cycle number, $k$ is the deactivation rate constant, $X_1$ is CaO conversion in the first cycle and $X_{ef\ r}$ is the residual conversion towards which conversion will converge asymptotically after a very large number of cycles. Best fitting parameters k and $X_{ef\ r}$ are collected in Table 2.

For comparison, data measured for the starting limestone are also included in Fig. 4. In general, it is observed that under CaL-CSP storage conditions (Fig. 4a) the multicycle effective conversions measured for the different samples are much higher than those obtained under CaL-$CO_2$ capture conditions (Fig. 4b). This is explained by the harsh calcination conditions used in $CO_2$ capture (high partial pressure of $CO_2$ and high temperature), which enhances CaO sintering as widely reported in previous works [6, 25, 50, 51] leading to a marked deactivation with the number of cycles. Moreover, the kinetics of carbonation is also remarkably affected by the type of conditions as Figure 5 illustrates. As well-known from previous studies [52, 53] carbonation takes place first through a fast reaction controlled phase on the free surface of the CaO particles, which is followed by a slower phase governed by the counter-current diffusion of $CO_3^{2-}$ and $O^{2-}$ anions across the carbonate product layer [54, 55]. As may be seen in Figure 5, carbonation in the fast reaction controlled phase is the major contribution to $CO_2$ uptake under CaL-CSP storage conditions. At these conditions carbonation in the solid-state diffusion phase is negligible whereas the fast reaction phase is enhanced by the high $CO_2$

partial pressure and high temperature used for carbonation. In contrast, carbonation in the solid-state diffusion controlled phase is relatively promoted under $CO_2$ capture conditions as reported in previous works [43]. The low $CO_2$ concentration (15% vol/vol) and lower carbonation temperature hinders the reaction kinetics while enhanced CaO sintering limits the maximum $CO_2$ uptake in this phase. CaL-$CO_2$ capture conditions lead also to the formation of a relatively thinner layer of $CaCO_3$ on the surface of the particles (between 40 a 60 nm) [53] as compared to carbonation conditions for CaL-CSP storage (~100 nm) [56], which would favor solid-state diffusion in the former case. As demonstrated in recent process simulation studies [57], this information on the carbonation kinetics is relevant to infer optimum values for important operation parameters such as the solids residence time in the carbonator.

**Table 2.** Best fitting parameters of Eq (3) to effective conversion experimental data for the composites and limestone samples tested under CaL-CSP storage and CaL-$CO_2$ capture conditions.

| | **CaL- CSP storage conditions** | | | **CaL-$CO_2$ capture conditions** | | |
|---|---|---|---|---|---|---|
| | ***Xef r*** | ***k*** | ***R²*** | ***Xef r*** | ***k*** | ***R²*** |
| **Raw Limestone** | 0.10 | 0.40 | 0.991 | 0.065 | 0.43 | 0.999 |
| **Milled samples** | | | | | | |
| **0wt $Al_2O_3$** | 0.16 | 0.09 | 0.999 | 0.082 | 0.35 | 0.999 |
| **5wt $Al_2O_3$** | 0.33 | 0.10 | 0.999 | 0.097 | 0.40 | 0.999 |
| **10wt $Al_2O_3$** | 0.35 | 0.19 | 0.998 | 0.073 | 0.29 | 0.997 |
| **20wt $Al_2O_3$** | 0.36 | 0.64 | 0.999 | 0.039 | 0.31 | 0.999 |

As can be seen in Fig 4, the effects of nanoalumina addition and milling are critically dependent on the type of CaL conditions employed. Thus, limestone milling yields a remarkable improvement of the multicycle activity under energy storage conditions (Fig. 4a). This could be explained by the decrease of particle size, which minimizes deactivation by pore-plugging. As reported in previous works, pore plugging is the main limiting mechanism under CaL-CSP conditions [23]. Comparatively, the beneficial effect of milling becomes weaker under $CO_2$ capture conditions (Fig. 4b). Under these conditions, enhanced sintering, caused by the harsh calcination conditions (high temperature and $CO_2$ concentration), is the main limiting mechanism and is not greatly affected by milling [34].

The addition of nanoalumina reduces initially the effective conversion in the first cycles due to the irreversible formation of calcium aluminates (as will be seen ahead in detail), which decreases the fraction of CaO available for carbonation. However, In the case of CaL-CSP conditions, the deactivation rate is notably reduced for the Al-composites as compared to the milled limestone alone (0wt $Al_2O_3$), and the residual effective conversion is substantially increased to a similar value for all the composites tested ($X_{ef\,r} \approx 0.35$), which is about twice that of milled limestone (Table 2). On the other hand, the beneficial effect of alumina addition is limited under $CO_2$ capture conditions to the 5wt $Al_2O_3$ milled composite. Under these conditions, a high alumina contents adversely affects the activity of the composite. In

accordance with previous reports [33, 58], an excessive $Al_2O_3$ content produces a decrease of the $CO_2$ uptake simply due to the considerable reduction of the active phase CaO. Furthermore, some authors have pointed out that the incorporation of $Al^{3+}$ aliovalent ions may add lattice defects in sorbent crystals that would promote sintering of the CaO grains [59].

Under both type of CaL conditions, the 5wt $Al_2O_3$ milled composite exhibits the best performance along the 20 cycles tested. To further analyze this point, Figure 6 shows the relative variation of $X_{ef}$ for this composite with respect to limestone milled alone. As can be seen, the relative improvement of performance for this composite is increased with the number of cycles under CaL-CSP storage conditions whereas it remains more or less stable from the first cycle under $CO_2$ capture conditions. This different behavior is explained by the diverse formation of calcium aluminates in both cases as described hereafter.

The effectiveness of the simple milling method employed in the present work can be further appreciated by a comparison of the performance of the 5%wt $Al_2O_3$ composite with that of other composites of similar composition but synthesized through more complex routes. Thus, our composite exhibits a $CO_2$ uptake of 0.41 g $CO_2$/g material after 20 cycles under CaL-CSP storage conditions, which is about the value reported by Obermeier et al. [42] for a synthetic composite with a molar ratio Ca/Al of 89/11 prepared by a more complex method such as liquid phase self-propagating high-temperature synthesis (LPSHS). Furthermore, our composite shows an enhanced performance compared to limestone when cycled under realistic CaL-$CO_2$ capture conditions (involving calcination at high $CO_2$ concentration and high temperature) whereas CaL conditions used in most of researches focused on Al-composites for $CO_2$ capture involve calcination under low $CO_2$ concentration atmospheres [58, 60].

### 3.2) Characterization of the composites after Ca-Looping cycles

#### 3.2.1) *X-Ray Diffraction*

Figures 7-8 show the powder X-ray diffractograms of the different composites after being subjected to the CaL cycles under CaL-CSP storage and $CO_2$ capture conditions, respectively. In both cases, the presence of crystalline calcium aluminates is clearly appreciated. As expected, the diffraction peaks of the calcium aluminates become sharper and more intense as the alumina content is increased, which is especially marked for the 20wt $Al_2O_3$ composite under $CO_2$ capture conditions (Fig. 8). These calcium aluminates were formed from the first calcination.

A main observation from Figures 7-8 is that two distinct types of calcium aluminate are formed under the different CaL conditions tested. A cubic structure of $Ca_4(Al_2O_4)_3O$ has been identified as the crystalline aluminate formed under CaL-CSP storage conditions. As far as we know, this crystalline phase has not been reported before for Al-composites subjected to calcium looping cycles. On the other hand, the crystalline aluminate phase formed under $CO_2$ capture conditions correspond to $Ca_3Al_2O_6$, which is in agreement with the aluminate reported by others authors [33, 60]. The robustness of these results has been confirmed by using another limestone from a different quarry. The Ca/Al ratio of the irreversibly formed calcium

aluminates is therefore determined by the type of CaL conditions being it higher for $CO_2$ capture conditions, which withdraws a larger amount of active Ca for carbonation.

It is interesting to note the different size of the CaO crystallites after CaL-CSP storage and CaL-$CO_2$ capture multicycle tests (Table 3). The crystalline CaO generated from the calcination of the different samples under CaL-$CO_2$ capture conditions presents crystallite sizes about three times larger than that of those generated under CaL-CSP storage conditions. The explanation lies in the harsh calcination conditions utilized in $CO_2$ capture, high partial pressure of $CO_2$ and temperature, which promote CaO sintering and crystallite growth [50].

**Table 3.** CaO crystallite size (L (nm) estimated for the CaO reflection peak (200) at $2\theta$ =37.4º) after the 20$^{th}$ cycle under CaL-CSP storage and CaL-$CO_2$ capture conditions. Estimated standard deviation for each value is included in parentheses.

| | **L (nm) Energy storage conditions** | **L (nm) $CO_2$ capture conditions** |
|---|---|---|
| | | |
| **0wt $Al_2O_3$** | 37 (5) | 53 (5) |
| **5wt $Al_2O_3$** | 17 (5) | 64 (5) |
| **10wt $Al_2O_3$** | 21 (5) | 60 (5) |
| **20wt $Al_2O_3$** | 22 (5) | 57 (5) |

The progressive formation of calcium aluminates as the number cycles increases occurs at different rates as depending of the CaL conditions employed. This has been checked in our work by preparing stoichiometric mixtures of $CaCO_3$ and $Al_2O_3$ (reactions (4) and (5), respectively) to produce the different kinds of calcium aluminates at CaL-CSP and CaL-$CO_2$ capture conditions,

$$4CaO + 3Al_2O_3 \rightarrow Ca_4Al_6O_{13} \quad (4)$$

$$3CaO + Al_2O_3 \rightarrow Ca_3Al_2O_6 \quad (5)$$

Figure 9 shows the X-ray diffractograms obtained after the 2nd calcination step under both types of CaL conditions. As may be seen, some CaO remains unreacted after calcination of the stoichiometric mixtures. However, it may be inferred from the peaks intensity that the amount of $Ca_3Al_2O_6$ formed after two calcination cycles under CaL-$CO_2$ capture conditions is much higher than the $Ca_4Al_6O_{13}$ amount formed under energy storage conditions. Additionally, $CaAl_2O_4$ is formed under $CO_2$ capture conditions in the stoichiometric mixture, following the reaction (6) [61]. Note that such crystalline phase was not observed in the composites tested (Figure 8).

$$Ca_3Al_2O_6 + 2Al_2O_3 \rightarrow 3CaAl_2O_4 \quad (6)$$

The formation of a large quantity of calcium aluminate at $CO_2$ capture conditions in the first cycles would be favored by the high calcination temperature employed (900 ºC). Thus, the formation of high amount of $Ca_3Al_2O_6$ at the beginning of the multicycle tests under CaL-$CO_2$

capture conditions could explain the relative variation of the effective conversion shown in Figure 6. Since most of the aluminates are formed from the first cycles, the relative variation of the effective conversion (Fig. 6) remains roughly constant along the cycles. On the other hand, $Ca_4Al_6O_{13}$ would be progressively formed with the number of cycles under CaL-CSP conditions, which would be related to the progressive increase observed for the relative variation of conversion (Fig. 6).

### 3.2.2) *SEM microscopy*

The samples cycled under energy storage and $CO_2$ capture conditions show evident morphological differences as seen in Figures 10 and 11, respectively. Such diverse CaL conditions produce on the CaO particles derived from limestone a well differentiated porous microstructure with pore sizes around 40 nm and 100 nm for CaL-CSP storage (Figure 10 a-c) and $CO_2$ capture (Figure 11 a-c) conditions, which is consistent with the observations reported in a previous work [39].

After the multicycle CaL tests at CaL-CSP storage conditions the surface of calcined milled limestone (0wt $Al_2O_3$) appears as a dense and cracked surface, with small grains and mesopores around 40 nm in size (Figure 10 a-c). Favorable conditions for carbonation in these tests (high $CO_2$ concentration and high temperature) lead to a quick built up of the $CaCO_3$ layer which, in addition to the relative small pore sizes generated during calcination (at the relatively low calcination temperature), hinders the $CO_2$ percolation into the inner grains of the CaO. This so-called pore plugging phenomenon is the limiting mechanism which is responsible for the activity loss under energy storage conditions as was shown in detail in previous works [23, 43]. After successive carbonation and calcinations, an external compact layer of CaO is generated, as observed in the corresponding micrographs (Fig. 10 a-c). In contrast, the calcined Al-composites after the cycles show a more porous and less sintered surface morphology. The calcined 5wt $Al_2O_3$ composite exhibit the least sintered particles, with macropores and cavities of size between 0.5 and 2 μm (Figure 10d). On the other hand, the surface of the calcined 20wt $Al_2O_3$ composite shows a higher proportion of nanoparticles and a marked decrease in the macropore size (Figure 10j). Modification of the pore size distributions through alumina addition could explain the different multicycle behavior of the different Al-composites. Thus, a lower proportion of alumina generates and preserves enough large pores during the CaL-CSP multicycle process, which inhibits pore-plugging as the formation of narrow pores is minimized. This observation could explain the higher effective conversion of the 5wt $Al_2O_3$ composite shown in Figure 4. A further beneficial effect of using less Al content is that less CaO is irreversible withdrawn to form calcium aluminates.

As seen in Figure 11, under CaL-$CO_2$ capture conditions, the addition of nanoalumina results in a large proportion of grains smaller than 500 nm as compared to the same sample after being subjected to CaL-CSP storage conditions (compare Figure 11i and Figure 10i for example). Furthermore, these small grains seem to block the pores of the CaO particles, which is more pronounced as the content of alumina is increased as clearly seen for the 20wt $Al_2O_3$ composite (Figure 11l). Moreover, the tortuous pore structure shown by this sample could hinder the diffusion of the $CO_2$ to the active sites within the particles. The importance of the

morphology and porosity of the sorbent for $CO_2$ capture has been already pointed out by other authors [25, 58, 62-64]. The loss of surface area and therefore capture capacity has been attributed to morphological changes due to the formation of calcium aluminates and sintering effects [40]. Many studies have evidenced that the $CO_2$ uptake of a sorbent is enhanced by large surface area values [52, 65], albeit it is influenced also by the pore network and tortuosity [58, 66].

### 3.2.3) *HRTEM microscopy*

Al-composites are characterized by two different nanostructure types as evidenced by the HRTEM micrographs in Fig. 12. Some of the CaO particles are formed by small grains of CaO ranging from 20 to 50 nm (Fig.12 a, b) whereas others are characterized by a smooth and uniform surface (Fig.12 c, d) showing a high Al content associated to calcium aluminate as revealed by the compositional mapping (Figure 13) . The size of the calcium aluminate particles is on the order of few nanometers up to 500 nm being found mainly at the periphery of the micrometric CaO particles of the composites as shown in Figures 13 and 14. This type of arrangement has not been clearly evidenced in previous works to our knowledge. Presumably, the steric hindrance of the formed calcium aluminates would mitigate sintering of the CaO grains along the CaL cycles, which might explain the observed enhancement of activity, especially under energy storage conditions. However, this steric hindrance could not be efficient enough to avoid the deactivation process of Al-composites under CaL-$CO_2$ capture conditions.

A HAADF-STEM mapping analysis of the distinct aluminate grains shows their different compositions as depending on the type of conditions either CaL-CSP storage (Figure 15) or CaL-$CO_2$ capture (Figure 16) conditions. The atomic ratio Ca/Al of the aluminate generated under CaL-CSP storage conditions is close to 0.67, which is consistent with the ratio of the $Ca_4(Al_2O_4)_3O$ observed from X-ray diffraction (Fig. 7). In contrast, the Ca/Al ratio of the aluminate obtained under $CO_2$ capture conditions is significantly higher and close to Ca/Al = 1.5, which matches the tricalcium aluminate $Ca_3Al_2O_6$ revealed by the XRD analysis (Fig. 8). Thus, the formation of $Ca_3Al_2O_6$ consumes a higher amount of available CaO as compared to $Ca_4(Al_2O_4)_3O$ which could explain the low activity of the composite 20wt $Al_2O_3$ under $CO_2$ capture conditions, as observed in Figure 4.

The formation of diverse calcium aluminate binders and microstructures under CaL-CSP storage and CaL-$CO_2$ capture conditions explains the different behavior of the Al-composites prepared in the present work as depending on the CaL conditions used. The simple milling pretreatment proposed could be economically viable for synthetizing large quantities of enhanced CaO-based sorbents as demonstrated by our results. However, a detailed study on the fluidization behavior of these composites and pellets obtained from them for their practical use in fluidized beds and cyclonic separators must be addressed in future works. Certainly, the particles used in our study are too small to be used in circulating fluidized beds, where optimum particle size is on the order of 100 μm [5]. For that purpose, pelletization of the milled powders would be required. We note however that the formation of calcium aluminates is expected to mitigate pore plugging as main limiting mechanism for the

multicycle activity at CaL conditions for energy storage [43]. At $CO_2$ capture conditions, sintering as main limiting mechanism does not pose a constraint to particle size in this range [53, 67, 68].

## 4. Conclusions

This work is focused on the Calcium Looping performance of $Al_2O_3$/CaO composites synthesized by mechanical milling of nanoalumina/limestone mixtures. It has been found that these composites exhibit different behaviors as depending on the type of CaL application, either for energy storage in CSP or for $CO_2$ capture, which has not been reported in previous works. The CaL performance of the composites can be rationalized from the diverse types of microstructure generated under CaL-CSP and CaL-$CO_2$ capture conditions due to the different carbonation and calcination conditions. Thus, calcination is carried out at high temperatures (>900 ºC) under high $CO_2$ concentration in the $CO_2$ capture application whereas it is performed at relatively moderate temperature (~ 700 ºC) under an inert gas for CSP energy storage. On the other hand, carbonation in the $CO_2$ capture application takes place at ~650 ºC under a 15%vol $CO_2$ concentration environment whereas it occurs at relatively high temperature (~850 ºC) under a high $CO_2$ concentration atmosphere for CSP energy storage. The formation of two distinct types of calcium aluminate as depending on the type of CaL conditions affects distinctly the microstructure and morphology of the CaO grains due to the steric hindrance effects of the aluminates. Thus, a calcium aluminate with ratio Ca/Al < 1 is formed under CaL-CSP storage conditions, which stabilizes the CaO microstructure and serves to mitigate pore-plugging as the main limiting mechanism under these conditions. Under CaL-CSP storage conditions, the residual effective conversion values are similar for the different Al-composites tested regardless of the $Al_2O_3$ content (in the range 5wt% to 20 wt%, $X_{ef\,r}$ ~ 0.35) and well above the residual conversion obtained for the limestone milled without additive ($X_{ef\,r}$ = 0.16). On the other hand, under CaL-$CO_2$ capture conditions, the crystalline phase $Ca_3Al_2O_6$ generated leads to a higher consumption of the CaO available, which yields a severe drop of the multicycle activity for the composites with larger than 5wt% Alumina. Only the composite with low $Al_2O_3$ content (5 wt%) yields a residual effective conversion value ($X_{ef\,r}$ = 0.097) higher than that obtained for the milled limestone ($X_{ef\,r}$ = 0.082). Therefore, it can be concluded that the 5wt% $Al_2O_3$ milled composite exhibits the best performance for prolonged cycles tests under both type of CaL conditions applied to CSP storage and $CO_2$ capture.

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