On the effect of inert support on the carbonation reaction of synthetic CaO-based CO₂ sorbents

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ABSTRACT

Calcium oxide has been proved to be a suitable sorbent for high temperature CO₂ capture processes based on the cyclic carbonation-calcination reaction. An intense work has been developed during the last years on the development of CaO-based synthetic materials aiming to reduce the CO₂ carrying capacity that suffers CaO derived from natural sorbents. Several synthetic sorbents have been prepared in this work with CaO contents between 40 and 95 % wt. on to two different inert supports MgO and Ca₁₂Al₁₄O₃₃. The effect of CaO content and inert nature on materials CO₂ carrying capacity and reactivity towards carbonation reaction has been assessed. The materials have been texturally characterised. A complete kinetic study has been performed and the Random Pore Model has been applied to determine the intrinsic rate parameters for the carbonation reaction. Suitable particles for operation in fixed bed reactor have been produced from some selected powdered materials, and a

complete particle reaction model that incorporate the intrinsic kinetic data has been developed and validated.

KEY WORDS: CO₂ capture, regenerable sorbents, carbonation, kinetics, limestone

INTRODUCTION

The separation of a pure CO₂ stream, combined with a well managed geological storage site is still considered to be a major mitigation option for climate change [1, 2]. The carbonation reaction serves as the basis for several high temperature CO₂ capture systems when it is coupled with a calcination step to produce a pure CO₂ stream. The use of the carbonation-calcination loop of CaO/CaCO₃ is now accepted as a viable technique for the capture of CO₂ in post-combustion [3, 4] or in pre-combustion [4, 5] routes. In this context, the sorption enhanced steam methane reforming (SER) arises as a novel intensified process that combines the H₂ production with inherent CO₂ capture [5] in a single system. In the SER process, the reforming, water gas shift (WGS) reactions, and the removal of CO₂ take place simultaneously in one single stage in presence of a catalyst and a CO₂ sorbent (Equation 1). The use of a calcium-based material allows the CO₂ to be removed from the gas phase as soon as it is produced, forming CaCO₃ [5-12]. According to thermodynamic predictions and experimental results, it is possible to obtain more than 95% vol. H₂ (on a dry basis) using CaO as sorbent [5, 6] in a wide range of temperatures from 923 K to 1023 K. The CO₂ sorption reaction (i. e. the carbonation of CaO) is exothermic and supplies “in situ” the heat required to carry out the endothermic reforming process.

As a product gas with almost pure H₂ is obtained directly from the reformer, the downstream purification process is simplified. The presence of sorbent minimizes the formation of coke allowing for a reduction of the steam excess in the reformer and the operation at lower temperature favours the use of cheaper materials in the reactor units [5, 6, 13-15]. Focused on combining hydrogen production and CO₂

1 separation, the use of CaO-sorbents in natural gas reforming or water gas shift processes was first
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3 proposed in the mid-90s [8, 16]. The inherent advantages associated to these concepts (namely higher
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5 hydrogen yields, process simplification or absence of water gas shift catalysts among others) have
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7 contributed to their great advancement in terms of materials development and conceptual process
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9 design, as reviewed by Harrison [5].
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14 With the objective of overcoming the decay in CO₂ capture capacity that present CaO based sorbents
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16 derived from natural limestones and dolomites, there has been an intense research in the recent years on
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18 the development of synthetic CaO-based sorbents, aiming for highly resistant to sintering materials with
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20 a sufficient CO₂ carrying capacity and reactivity to sustain CaL processes see for example the reviews
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22 by Liu et al. [17] and Erans et al. [18]. Different strategies have been adopted according to the literature
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24 to produce synthetic CaO-based sorbents as for example the use of sintering-resistant calcium
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26 precursors as nano-sized CaO/CaCO₃ [19], organometallic precursors [20, 21] or precipitated CaCO₃,
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28 whose reported results largely varied with the test conditions. Their performance has been related with
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30 their differences in pore structure/surface area, but not systematic analysis has been performed [17].
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32 Sorbent doping has been also proposed as a method to improve the stability of CaO based sorbents
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34 without successful results [22, 23], but it is the incorporation of CaO to an inert matrix the most
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36 extended and deeply tested strategy [17, 24-31]. This strategy was derived from the expertise on
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38 dispersing active components on to porous inert matrix to synthesise diverse sorbents and catalysts, and
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40 it was supported by the observation of the better performance in terms of cyclic stability that presented
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42 calcined dolomites when compared with calcined limestones. The MgO in calcined dolomites would
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44 help to hinder the CaO/CaCO₃ sintering along cycling [8, 16, 32]. Since Ahiara et al.[33] incorporated
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46 CaO to an inert CaTiO₃ matrix to react with CO₂, an important range of supports as for example MgO,
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48 MgAl₂O₄, Ca₁₂Al₁₄O₃₃, SiO₂, and ZrO₂ among others have been evaluated. Some of them were able to
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50 reduce the sintering of CaO grain with temperature, and improved the cyclic reactivity of the sorbent.
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52 Also a various techniques have been developed for their production, as for example sol-gel combustion
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as a popular approach to produce nanomaterials, and a common route when mixed the CaO precursors with aluminium precursors to produce $\text{CaO-Ca}_{12}\text{Al}_{14}\text{O}_{33}$ materials, as CaO will react with Al_2O_3 after calcination [27-29, 34]. Mixing on its different approaches has been also a common production route: dry mixing when all the precursors are mixed in dry form; suspension mixing of insoluble precursors in a solvent to be dried to form a powdered product [30]; hydrothermal route when mixed the solid precursors in water and then brought to an autoclave at mild temperature and moderate pressure to form an hydro garnet that it is later calcined [35]; sol mixing when at least one of the precursors is soluble [27-29, 34, 36, 37], and wet mixing when both precursors are soluble in the solvent and they are subsequently processed to form a dry product [38, 39]. A common procedure to evaluate the performance of a given CO_2 sorbent is to evaluate the evolution of its CO_2 carrying capacity (mole basis expressed as moles CO_2 captured per mol of CaO in the material, or weight basis expressed as weight of CO_2 captured per weight of calcined sorbent) along multiple calcination/carbonation cycles [33, 40-44]. However, it is necessary to highlight that the evolution of sorbent CO_2 carrying capacity and the long term performance of the materials can be affected by the experimental conditions during the testing of the materials, not only due to the possible sintering phenomena that will take place in more or less extension depending on the calcination conditions (in terms of CO_2 partial pressure, presence of steam and temperature during calcination stage) [45-47] but also due to the partial reactivation of the sorbent that takes place when the carbonation reaction is extended beyond the fast reaction stage [43, 48, 49]. In this way, it is not possible to compare the performance of materials tested under diverse reaction conditions, but, there are some valid trends that can be derived from the data in the literature. As for example, according to the experimental results compiled by Liu et al. 2012[17], the maximum CO_2 capture capacity of a sorbent is directly proportional to its CaO loading. According to the three dimensional percolation theory, these authors proposed that the maximum CaO content that can be allocated in a continuum framework of inert support was 82.77 % wt. [38]. The stability and high efficiency CaO utilisation that presented materials with CaO contents between 52% to 75% weight was attributed to the fine dispersion of CaO in the sorbent that presented nanocrystalline domains of MgO

adhered to their surfaces. In this way, co-precipitation could be a suitable synthesis method to produce highly dispersed CaO on to inert support. This was the case of materials obtained by Filitz et al. [50] , Kierzkowska et al. [51] and Zhenissova et al. [31] that were prepared through co-precipitation of Ca containing salts for the active phase, and Mg or Al containing salts for the inert support to obtain the mixture of Ca^{2+} and Mg^{2+} or Al^{3+} in the crystalline lattice. The authors reported a good stability of the materials along several calcination/carbonation cycles.

As shown in the introduction section, there has been intense work on determining the effect that inert support has on the reactivity stabilization of synthetic sorbents [17, 25, 26, 52], and although there is a growing interest on modelling the reaction of synthetic CO_2 sorbents and bi-functional CaO-based materials [53, 54], there is scarce work on the determination of synthetic sorbent reaction kinetics, and on the effect that the inert support and CaO load have on the carbonation reaction of CaO [55, 56]. In this way, the present work aims to determine the effect that inert support type and/or preparation method and CaO content might have on the intrinsic kinetics of the carbonation reaction of CaO. The present work is focussed on materials that contain MgO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ as inert supports. It will also incorporate textural characterisation and analysis of the reactivity of particles produced with the synthesised powders (0.6-1 mm and 1-2 mm particle size cuts). Finally a particle reaction model that has been successfully applied to describe the carbonation conversion with time of CaO-natural based sorbent that have experienced multiple calcination/carbonation cycles has been extended to incorporate the effect of particle size, building in this way a complete particle model that incorporate the effect of diffusion phenomena to the interior of the particles.

EXPERIMENTAL

Synthesis of CaO-based CO_2 sorbents

Two different synthesis routes have been used to produce CO_2 sorbents, aiming to disperse the Ca onto an inert support to reduce the typical sintering of natural CaO based sorbents along multiple calcination/carbonation cycles. The first synthesis route aims the production of materials that emulate

the structure of natural occurring dolomites in which the MgO, inert for the carbonation reaction in the range of temperatures of interest, acts as a stable framework [38, 50]. In the second route, mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) will act as inert support. and calcium aluminate cement in different proportion is used as binder and alumina source. The alumina present in the cement will partially react with CaO during calcination to generate $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ that has proven to be an excellent support for synthetic CO_2 sorbents [30, 57].

In this way, synthetic dolomite sorbents with different CaO:MgO molar ratios were prepared following a co-precipitation route [50]. Calculated amounts of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in deionised water with a total concentration of 3 M. A 2M solution of $(\text{NH}_4)_2\text{CO}_3$ was used as precipitation agent and added drop wise to the mixture under vigorous stirring at room temperature. A pH value of 9 was kept constant by the drop wise addition of 30 % NH_3 aqueous solution. The precipitates were aged for 2 hours and subsequently washed with water while vacuum filtration. The filter cakes were then oven-dried at 120 °C for 12 hours and calcined in a muffle furnace in air at 875 °C for 2 hours. Four sorbents with different active phase to support molar ratios (5:1, 3:1, 2:1, 1:1, 1:2), and also pure CaO, were prepared. Fresh calcined materials were crushed and sieved to obtain a powder with a particle size less than 100 μm .

In the second synthesis route, natural limestone and calcium aluminate cement were used as raw materials for preparing the synthetic sorbent [44, 57]. First, natural limestone was calcined for 2 hours at 900°C, producing 55.59 wt.% of solid residue. Main components of calcined limestone were 97.85 wt.% of CaO, 0.19 wt.% of MgO and 1.92 wt.% of Na_2O . Calcium aluminate cement is a commercial product from cement industry mainly composed of aluminium, iron and calcium oxides. The materials were mechanical mixed in the correct proportions to obtain CaO contents between 60-95 % wt. Afterwards, water was added drop wise with a continuous mixing to produce a homogeneous paste that was dried in a furnace at 120 °C for 12 hours, then it was crushed and sieved to obtain a powder with a particle size less than 100 μm , finally the powder materials were calcined in air at 900 °C for 2 hours.

Some selected materials were processed through an agglomeration process using a polyethylene glycol (PEG) 10 % wt. aqueous solution as binder. The objective was to produce sorbent particles suitable for operation in a pressurized fixed bed reactor, as it would be the case of the H₂ production process via Ca/Cu chemical loop. Briefly, the powdered materials were mixed by a propeller working at 2000 rpm and binder was added drop wise up to a 35 % of total (solid + binder) weight. Particles were dried at 120 °C overnight and sieved to separate fractions with different particle diameter. Two particle size fractions (0.6-1 mm and 1-2 mm) were selected and calcined in air at 900 °C during 1 hour.

Characterization of CaO-based CO₂ sorbents

Sorbents were deeply characterized in order to determine textural, physical, and crystallographic parameters that can influence the CO₂ carrying capacity and mechanical stability of the materials. In order to avoid hydrated and/or carbonated species all samples were calcined immediately before characterization at the same conditions that were used during the synthesis procedures and were stored in a desiccator. Surface area was determined by nitrogen adsorption at -196 °C in a Micromeritics ASAP-2020 analyser. Prior to the N₂ adsorption analysis, each sample was degassed at 250 °C for approximately 3 h. The Brunauer-Emmett-Teller (BET) model was used to calculate the surface area in the P/P₀ range of 0.02 to 0.3. A picnometer AccuPyc II 1340 was used to determine sorbents density by measuring the amount of He displaced by the sample. Prior to the analysis, each sample was degassed at 130 °C in a vacuum oven. In order to estimate the solid porosity (ϵ) and the solid pore size distribution, a Hg Porosimeter Quantachrome Pore Master analyser was used. The crystallinity and phases composition of the synthesized sorbents were determined using X-ray powder diffraction (Bruker, AXS D8 Advance, Cu K α radiation, equipped with a Lynxeye superspeed detector operated at 40 mA and 40 kV). Each sample was scanned in the 2θ range of 15-80°. The step size was 0.02° and the scan time per step was 3 s. Particles were grinded to powder before analysis. XRD diffractograms not only allowed for phase identification but also its quantification. Rietveld analysis of the diffractograms allowed for quantification of different phases present in the sorbents. In order to check the accuracy of these measurements selected samples were also quantified by ICP-AES and a good correlation between both

techniques was observed for Ca and Mg real concentrations. To define the morphology of sorbent particles (surface and cross-section), a scanning electron microscopy (SEM) using a Hitachi S-3400 N was applied. In addition, energy dispersive X-ray (EDX) analysis was used to evaluate the distribution of the different elements present in the sorbents.

Material reactivity and cyclic stability tests were performed using a TGA analyser. Briefly, the apparatus consists of a quartz tube with a platinum basket suspended from it, inside a two-zone furnace. The furnace can be moved up and down by means of a pneumatic piston. The position of the furnace with respect to the platinum basket allows alternation between calcination and carbonation conditions. The temperature and sample weight were continuously recorded on a computer. The reacting gas mixture can be regulated by mass flow controllers and fed in through the bottom of the quartz tube. Steam was generated by external electric heating of the water flow controlled by a liquid mass flow controller and then introduced into the reaction atmosphere. The evolution of sorbents CO_2 carrying capacity was assessed through the following routine: each sample was carbonated for 15 minutes in 15vol.% CO_2 /15% H_2O /70 vol.% N_2 at 650°C up to reach at least 50 calcination-carbonation cycles. The sorbent calcination was performed at 900 °C in a 70%v. CO_2 in air. To perform the kinetic study, about 2 mg of material was introduced in the platinum sample pan. The effect of CO_2 partial pressure, carbonation temperature and particle size on the evolution of CaO conversion with time was assessed.

Characterization results

Main textural and physical properties of sorbents prepared by the co-precipitation method are presented in Table 1. Pure CaO shows the lowest surface area, density and porosity whilst the synthetic dolomites with a ratio 1:1 and 1:2 present the highest values. The presence of MgO inert phase seems to favor the development of a rich structure with surface areas ranging from 16 m^2/g to 28 m^2/g , higher than that of natural CaO (12-15 m^2/g) and high porosities ranging from 0.75 to 0.84. These results are in line with other well dispersed CaO-MgO materials published by several authors and using different preparation methods like wet-mixing (up to 25 m^2/g) [38], co-precipitation (2-35 m^2/g) [11], sol-gel

auto-combustion (28 m²/g) [58]. The agglomeration process reduces both the surface area (12 m²/g) and the porosity of the materials (0.5), moderating the benefits, in terms of textural properties, obtained for the co-precipitated materials.

Table 1. Main textural and physical properties of sorbents prepared with the co-precipitation method.

Sorbent	S _{BET} (m ² g ⁻¹)	Particle density (gcm ⁻³)	ε	CaO crystallite size(nm)	MgO crystallite size (nm)
CaO	15.6	2.21	0.53	-	-
CaO:MgO 5:1	16.7	2.94	0.76	32.5	16.2
CaO:MgO 3:1	17.5	3.19	0.78	38.5	19.6
CaO:MgO 2:1	16.5	3.24	0.75	39.9	22.8
CaO:MgO 1:1	25.9	3.28	0.75	36.9	15.9
CaO:MgO 1:2	27.7	3.15	0.84	33.8	19.8
CaO:MgO 2:1 0.6-1.0 mm	12.2	3.14	0.50	-	-
CaO:MgO 2:1 1.0-2.0 mm	11.9	3.05	0.51	-	-

The existing crystalline phases in the co-precipitation CO₂ sorbents were determined by X-ray Diffraction. Figure 1 (left) illustrates the X-ray diffraction patterns of selected CaO sorbents with different CaO:MgO molar ratios. All samples presented the characteristic reflections of CaO and MgO along with low intensity peaks of Ca(OH)₂ phase that are attributed to the absorption of moisture due to the hygroscopic nature of the materials. Rietveld analysis of the diffractograms followed by Double-Voigt approach allowed to calculate the crystallite size of CaO phase, that was ranging between 32 and 40 nm, and MgO phase ranging from 16 to 23 nm (see Table 1). These results are comparable with other recently published by different authors and using different synthesis methods. Liu et al. [10] published well dispersed CaO-MgO materials prepared through wet-mixing of calcium gluconate and magnesium gluconate salts showing the formation of CaO particles of 36 and 120 nm, with nanocrystalline

domains of MgO (9 and 50 nm). Antzara et al. [58] have also recently published the preparation of CaO-MgO sorbents by sol-gel auto-combustion method with a CaO crystallite size of 29.5 nm.

Figure 1. X-ray diffraction patterns of selected CaO sorbents with different CaO:MgO molar ratios (left) and selected CaO/calcium aluminate cement sorbents with different CaO % wt (right).

Figure 2 shows the SEM micrograph of a particle cross-section corresponding to the synthetic dolomite CaO:MgO 2:1 with a particle size of 1.0-2.0 mm. Indicative mapping of the surface composition with EDX was performed on the same samples and is also presented in Fig. 2. The analysis confirmed the good distribution between Ca and Mg elements, indicating the suitability of the followed synthesis route for uniform dispersion of CaO and inert support in the solid particles. Thus, the finely-dispersed support among CaO particles would fully function as the metal matrix, which could effectively prevent the collapse of pore structure and further suppress the sintering of sorbent particles.

Figure 2. Cross-section SEM micrograph (center) and EDX analysis (left Ca, right Mg) of particulate CaO:MgO 2:1 material.

Figure 3 shows some examples of the pore size distribution for the fresh calcined materials synthesized and tested in this work. The synthetic dolomites (figure 3 left) reported high and similar porosity (shown in Table 1), however they present differences on the pore structure. All of them present an important pore volume in the range of pore diameters below 50 nm, that according to the literature [59, 60] are typical pore diameters meaningful for reaction of CaO with CO₂, but these materials, specially the material with lower CaO content, present an important pore volume at higher pore diameters that could be associated with the presence of MgO as it was found by Liu et al. [38]. The data obtained from Hg porosimetry will serve to determine the materials structural parameter that will be incorporated in the reaction model.

Figure 3. Pore size distribution of the fresh materials, calcined at 900 °C in air. (Left) selected CaO sorbents with different CaO:MgO molar ratios and (Right) selected CaO/calcium aluminate cement sorbents with different CaO % wt.

Main textural and physical properties of sorbents with particle size ranging from 0.6 to 1 mm prepared by the mechanical mixing method are presented in Table 2. These materials present a less developed surface area and porosity compared with the synthetic dolomites (see table 1 for comparison). A higher fraction of calcium aluminate in the material results in lower BET surface area and this can be related with the existence of intermediate crystalline species that contain CaO and Al₂O₃ on their structure.

Table 2. Main textural and physical properties of sorbents prepared by the mechanical mixing method, particle size cut 0.6-1 mm except for powder that is less than 0.1 mm.

Sorbent	S_{BET} (m^2g^{-1})	Particle density (gcm^{-3})	ϵ
90% wt. CaO powder	14.25	3.10	0.64
90% wt. CaO	10.17	3.12	0.56
80% wt. CaO	8.55	3.13	0.53
60% wt. CaO	7.11	3.16	0.54

The $\text{CaO-Ca}_{12}\text{Al}_{14}\text{O}_{33}$ materials present a higher mean pore diameter, around 100 nm, (Fig. 3 right) than CaO-MgO materials, that might be linked to their synthesis method as the CaO source in these materials is obtained from the calcination of powdered natural limestone. In this way, pore size distribution of the materials with a high CaO content is very similar to those that present natural lime [59, 60] while the materials with higher inert content present a wider pore size distribution peaking at higher pore sizes. This fact might be associated to the increment of intermediate species other than $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and CaO that appear in the XRD diffractogram of sample 60% wt. CaO compared with the one of sample 90% wt. CaO where only CaO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ phases are detected (see figure 1, right). The Figure also includes the results obtained for a 90% wt. of CaO sample that has experienced 15 calcination/carbonation cycles. It can be observed that the mean peak around 100 nm has been reduced and a shoulder around 200 nm is starting to appear due to the shrinkage of the porous during the sintering process. This can be also reflected on the reduction of its surface area from 10.17 to 5.48 m^2g^{-1} pointed out by the growth of the CaO crystallites from 64.7 to 76.4 nm.

RESULTS

The present work has been focussed on determining the effect that the amount of active phase for the carbonation reaction and the nature of the support might affect to the material chemical stability and reactivity. In this way, in a first step to determine the performance of the materials, the evolution of CO_2 carrying capacity with the number of reaction cycles under meaningful reaction conditions for the

process has been evaluated (experimental conditions detailed in the experimental section comprised the presence of steam during the carbonation stage and high CO₂ partial pressure during calcination stage). Figure 4 compiles the experimental results on the evolution of CO₂ carrying capacity with the number of calcination/carbonation cycles for the materials prepared through both synthesis routes (left CaO:MgO co-precipitated materials, and right CaO-Ca₁₂Al₁₄O₃₃ mechanically mixed-calcined materials), for CaO contents between 40 to 90 % wt. The figures also include for comparison the chemical stability of a 100 % wt. CaO material prepared by co-precipitation, and CaO obtained directly from the calcination of natural limestone. According to the Figure in the left, the presence of MgO really improves the CO₂ carrying capacity of the materials in the long term performance. This can be extracted from the comparison between the series obtained with the precipitated CaO and the rest of the materials that contain CaO:MgO. Among these last materials, it can be observed that the decay trend in CO₂ carrying capacity along the initial cycles is reduced for the materials with higher MgO content (especially materials CaO:MgO with a molar ratios 1:1 and 1:2). This observation is coherent with the results presented by Li et al. [25] that applied the Zener pinning theory to describe the inhibition of CaO grain sintering thanks to the addition of an inert support. According to those authors, the sintering inhibition effect is dependent on the inert support size, and also on its volume fraction. In this way materials with a relatively high inert content would present a lower amount of active CaO during the initial cycles, but their decay in activity would be reduced with respect to materials with lower amount of inert support. As an example for the sorbents tested, the CaO/MgO 1:2 material presents a 75 % wt. CaO utilization at cycle 40 after 15 minutes of reaction, while only 35 % wt. of the CaO present in the CaO/MgO 5:1 is useful for the carbonation reaction within this 15 minutes of reaction. Still it is important to highlight that the lifetime of these materials will comprise an important number of reaction cycles, and at this point the differences between materials disappear and, as long as there is a minimum amount of inert (for example 12.5 wt. % in the material CaO/MgO molar ratio 5:1), the sorbent performance is highly improved with respect to the material with no inert support.

Figure 4. (Left) Evolution of CO₂ carrying capacity with the number of reaction cycles for the co-precipitated materials. (Right) Evolution of CO₂ carrying capacity with the number of reaction cycles for the mechanically mixed materials (particle size cut 0.6-1 mm). Carbonation 15 minutes in 15vol.% CO₂/15% H₂O/70 vol.% N₂ at 650°C. Calcination at 900 °C, 70%v. CO₂ in air.

Figure 4 on the right, shows a similar comparison but for the materials prepared by mechanical mixing and later calcination of CaO and Ca cement aluminate. A similar trend, as for the co-precipitated materials, is observed with a minimum amount of inert support required to maintain sorbent activity. In this case it is clear that the activity of the material with a 5 % wt. cement aluminate is very similar to that obtained with natural lime. Comparing both types of materials, the CO₂ carrying capacity of materials prepared through co-precipitation, is sensible higher than for the CaO-Ca₁₂Al₁₄O₃₃ materials. This could be related with the higher crystallite size (over 65 nm) that presents CaO in the CaO-Ca₁₂Al₁₄O₃₃ solids with respect to the 30-40 nm crystallite size that present the co-precipitated materials [25], and also with the presence of intermediate phases CaO·Al₂O₃ in the materials with higher amounts of Ca cement aluminate in the mechanical mixing prepared sorbents. Commonly the experimental data on evolution of CO₂ carrying capacity are fitted to diverse semi-empirical expressions that allow estimating the material activity in the long term [61]. In this work the experimental data have been fitted to Equation (1) that has been widely used in the literature to describe the evolution of sorbent CO₂ carrying capacity with the number of cycles [62]. In this work, the expression that is analogue to a second-order catalyst deactivation equation adapted to consider the proportionality between conversion,

surface area and product layer thickness through two parameters that are characteristic of every material: the sorbent deactivation constant, k , and sorbent residual capacity X_r , allows estimating the mol CaO reacted/mol of sorbent that the material is able to capture at a given number of cycles. To determine realistic parameters for the sorbents synthesised, two of them (shown in Figure 5) have been selected to be tested for a long number of cycles (up to 100 cycles). The values obtained were $k=1.15$ and $X_r=0.31$; $k=0.25$ and $X_r=0.22$ for the CaO-MgO and CaO-Ca₁₂Al₁₄O₃₃ materials respectively. According to the CO₂ carrying capacity shown in the long term, both materials would fulfil the requirements described by Fernandez et al. [63] to sustain a Sorption Enhanced Steam Methane Reforming process at large scale.

Figure 5. Long term CO₂ carrying capacity for the two selected materials. Experimental data have been fitted to Eq. (1). Particle size cut, 0.6-1 mm. Carbonation 15 minutes in 15vol.% CO₂/15% H₂O/70 vol.% N₂ at 650°C. Calcination at 900 °C, 70%v. CO₂ in air.

These two materials have been selected to produce sorbent particles in two different particle size cuts 0.6-1 mm and 1-2 mm, and will serve to validate the particle reaction model developed in this work. To

1 start, a complete kinetic study has been performed on the materials synthesised, aiming to determine the
2 kinetic parameters governing their conversion during reaction with CO₂. To do so, the effect of
3 operation variables as reaction temperature, CO₂ partial pressure and particle size on CaO conversion to
4 CaCO₃ have been evaluated as well as the effect of CaO content and inert support.
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11 The following paragraphs will be dedicated to determine the intrinsic kinetic parameters of the synthetic
12 sorbents and to determine how the effect of CaO content and inert support might affect them. In general,
13 the experimental results that will be shown in the following pages follow the expected trends from CaO-
14 based sorbents with respect to the operational variables named above Figure 6 shows an example of the
15 effect of carbonation temperature on the CaO molar conversion of the CaO-MgO 2:1 material in powder
16 form (left figure focus on the initial reaction stage and right figure shows the data for extended reaction
17 time), where it can be observed the well known two reaction stages [16, 41, 55, 56, 64-67] related with
18 the control by the chemical reaction during the initial reaction stage, followed by a second slower
19 reaction stage which is governed by a combined control between the chemical reaction and the CO₂
20 diffusion through the product layer formed [60, 65, 68]. From the figure on the left it can be also
21 observed the low dependence with temperature that presents the slope of the conversion curves during
22 the fast reaction stage. The figure on the right shows the evolution of CaO molar conversion for longer
23 reaction times, and from this figure it can be observed during the combined controlled regime there is a
24 more important dependence with temperature (data up to 150 s). Finally for longer reaction times, there
25 is a smoother variation in the slope of CaO conversion curves that might be associated with a well
26 developed CaCO₃ product layer where the carbonation kinetic constant no longer affects the reaction
27 rate[65]. Finally the materials reach the maximum CaO conversion according to their composition.
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Figure 6. Effect of reaction temperature on CaO carbonation conversion, $p\text{CO}_2$ 10 kPa. right) focussed on short reaction times; left) focussed on extended reaction times. Material CaO/MgO 2:1 molar ratio.

Figure 7 shows an example of the effect of CO_2 partial pressure on CaO molar conversion curves (X_{carb}), and according the Figure 7 left, which shows the average reaction rate during the fast reaction period as function of CO_2 partial pressure, and particle size, the carbonation reaction is first order with respect to the CO_2 concentration. From this figure it can be observed that the reaction rate decreases with increasing particle diameter, indicating that the CO_2 diffusion towards the interior of the sorbent particle plays a role in particles size cuts 0.6-1 mm and 1-2 mm, in these cases the homogeneous reaction pattern proposed for finer particles[66] will be no longer valid for the materials in particle form suitable for operation in fixed bed reactor.

Figure 7. left) Average $\Delta X / \Delta t$, for the fast reaction stage, versus concentration gradient, for the different particle size cuts; right) Carbonation conversion curves (CaO molar conversion) for the material with

ratio CaO/MgO 2:1, powder, at 650 °C two different CO₂ partial pressures. Lines represents model predictions.

Figure 7 right) shows an example of CaO conversion curves at two different CO₂ partial pressures for the material CaO/MgO 2:1 in powder form. On view of the results in Figure 7 left), this work will put an effort on including the effect of particle size on the sorbent conversion model allowing in this way to model the carbonation reaction of sorbent particles with sizes suitable for fixed bed operation. To model and predict the evolution of CaO conversion with time, the Random Pore Model that has been previously used to model the carbonation reaction of CaO based sorbents in multi-cycle operation has been selected [56, 66]. The experimental data obtained from the testing of the materials in powder form will serve to determine the intrinsic kinetic parameters as radial diffusion resistances through the pore network of the particle can be neglected for fine sorbent particles and the materials can be assumed to be reacting following a homogeneous reaction pattern. The kinetic parameters determined will be incorporated into a complete particle reaction model that includes the effect of transport phenomena in the materials pore network. This particle model will be validated with the experimental data obtained with the bigger particle size cuts.

To determine the kinetic parameters for the carbonation reaction, the general expression for the instantaneous solid-gas local reaction rate developed by Bathia and Permuter, [69] Equation (3), suitable to describe the carbonation reaction rate of a porous system in the presence of product layer diffusion resistance has been simplified and integrated under two different scenarios. For the situation where the chemical reaction controls the carbonation the parameter β (Equation 4), that shows the relation between the kinetic constant (k_s) and the apparent diffusion coefficient $D_{p,}$, tends to zero and therefore Equation (3) can be simplified and integrated to obtain Equation (5) that allows predicting the evolution of CaO conversion (X_{carb}) with time.

$$\frac{dX_{carb}}{dt} = \frac{k_s}{1 + \beta} \left(1 - X_{carb} \right) \quad (3)$$

$$\frac{X_{carbN}}{X_{max}} = \frac{k_s}{k_s + D_p} \quad (4)$$

$$- \frac{X_{carbN}}{X_{max}} = \frac{k_s}{k_s + D_p} \quad (5)$$

The second scenario corresponds to the limit of product layer diffusion control, where k_s/D_p tends to infinity and Equation (3) can be integrated to the limiting form:

$$- \frac{X_{carbN}}{X_{max}} = \frac{k_s}{k_s + D_p} \quad (6)$$

D_p being the apparent product layer diffusion coefficient that is also related to the effective diffusion coefficient, D , as follows:

$$\frac{D_p}{D} = \frac{1}{1 + \frac{k_s}{D_p}} \quad (7)$$

The model that has been adapted to the characteristics of the materials synthesised, in this way, X_{carb} in the equations above refers to the CaO molar conversion considering materials composition (this is mol CaO converted/mol material), the parameter Ψ is $4\pi L_0(1-\varepsilon)/S_0^2$, where L_0 , S_0 and ε can be obtained from the Hg porosimetry data from the raw calcined materials [65, 66, 69]. The evolution of these textural properties with the number of reaction cycles has been related proportionally with the evolution of the ratio X_{carbN}/X_{max} , where X_{carbN} can be extracted from the fitting of Equation (1) [66] and X_{max} corresponds to the maximum CaO molar conversion according to its composition, and ρ is the material density referred to CaO (kg CaO/m³ material). Expressions 5 and 6 were used to derive the intrinsic kinetic parameters for the carbonation reaction by representing left hand side terms of those equations vs. time or the root of time to determine k_s and D_p respectively. Figure 8 shows an example of the results, from which in the figure on the left, the Left hand side in Equation (4) has been plotted against time. Therefore from the initial part of the slope in Figure 8, k_s for each experiment can be calculated. Figure 8 right shows an example of the representation of left hand side term in Equation (5) vs. the root of time. From the slope of the second part of the curve, the apparent diffusion coefficient, D_p , and

therefore the effective product layer diffusion coefficient, D , have been estimated. This exercise has been performed and individual values of k_s and D have been obtained for all the materials synthesised.

Figure 8. (Left) Representation of calculated left hand side term of Equation (5) vs. time for an experimental conversion curve. (Right) Representation of calculated left hand side term of Equation (6) vs. the root of time for an experimental conversion curve.

Trough the representation of the experimental data of materials with different amount of CaO under identical conditions of carbonation T and CO_2 partial pressure (Figure 9), it can be observed that the main differences between CaO conversion curves is the conversion level at which the transition between the two different reaction rates (or regimes) takes place. Then a fitting exercise that involved all synthetic dolomites tested with CaO:MgO ratios 5:1, 2:1, 1:1 and 1:2 in powder form ($d_p < 100 \mu\text{m}$) was performed to determine the kinetic parameters that could be valid to describe the carbonation reaction of materials regardless their CaO content. An Arrhenius representation was plotted for individual values of k_s and D . From the slope and the ordinate in the origin, k_{s0} (m^4/kmols) and E_{aK} (kJ/kmol) and D_0 (m^2/s) and E_{aD} (kJ/kmol) were determined for the materials synthesised.

$$k_s = k_{s0} \exp(-E_{aK} / RT); \quad k_s (\text{m}^4/\text{kmols}) \quad (8)$$

$$D = D_o \exp(-E_{aD} / RT); \text{ with } D \text{ (m}^2\text{/s)} \quad (9)$$

Figure 9. Carbonation conversion curves for materials with different ratio CaO/MgO, at 650 °C and $p\text{CO}_2$, 15 kPa. Left) Zoom to the initial seconds of reaction. Right) complete conversion curve when the product layer is well developed.

The transition between reaction regimes, has been associated to the formation of a product layer of CaCO_3 , and the variation in reaction rate could be justified via two mechanisms: the effect of a variable product layer diffusion resistance that increases, as the product layer thickness increases (this was confirmed in the case of Mess et al. [70] for thick product layers) or alternatively, the initial formation of CaCO_3 islands on the free surface of CaO which grow until the individual CaCO_3 grains coalesce to form a CaCO_3 product layer that is able to seal the free CaO surface [66]. In both mechanisms, there is reason to believe that diffusion reaction control starts to take effect (through the effective CO_2 diffusivity) only after a certain level of product layer thickness has been reached. In both mechanisms, CO_2 diffusion is very fast and does not affect the progress of carbonation for low conversions (low product layer thickness). From a practical point of view, both mechanisms can be simplified and represented in the same form: an initial reaction stage controlled by the kinetic constant and a second stage where both the diffusion coefficient and kinetic constant control the progress of the carbonation

reaction. Then, the CaCO_3 product layer thickness at which this abrupt change in reaction rate takes place can be estimated directly from the textural characterisation of the materials and the experimental CaO conversion curves. By applying the model developed by Alvarez and Abanades [60], the evolution of particle conversion with product layer thickness can be estimated, for a material with a given pore size distribution according to Equation (10):

$$\frac{\Delta V^{\text{cum}}}{V_p} = \sum_i \frac{4\pi R_i^3 \delta_i}{3V_p} \left(\frac{h_i}{R_i} \right)^3 \quad (10)$$

where ΔV^{cum} is the delta volume from direct Hg mercury porosimetry, R_i is the pore radius for every pore interval, δ_i corresponds to the decrease in pore radius upon carbonation, and h_i is the product layer thickness at every pore interval. The decrease in pore radius during carbonation was estimated from geometrical considerations and can be related to pore radius, product layer thickness and α , according to:

$$\delta_i = R_i \left(1 - \alpha \right)^{1/3} \quad (11)$$

The parameter α corresponds to the volume fraction of carbonate invading the former volume of pore i , and can be calculated from the molar volumes of CaO ($16.9 \cdot 10^{-3} \text{ m}^3/\text{kmol}$) and CaCO_3 ($36.9 \cdot 10^{-3} \text{ m}^3/\text{kmol}$) according to:

$$\alpha = \frac{V_{\text{CaO}}}{V_{\text{CaO}} + V_{\text{CaCO}_3}} \quad (12)$$

When the small pores are filled up, the product layer thickness becomes: $h_{k-D} = \frac{R_k}{\alpha}$; h_{k-D} being the critical product layer thickness found in Alvarez and Abanades [60]. By applying this model to the pore size distributions obtained from the materials in Figure 1, and considering the experimental conversion at which transition between reaction regimes take place, an average product layer thickness of 5, 25, 60 and 80 nm has been considered as the product layer thicknesses that determines the

transition between reaction regimes for the CaO-MgO 2:1, 1:1, 2:1 and 5:1 respectively. On view of these results, the effective product layer thickness that marks the transition between reaction regimes is the parameter mostly affected by the CaO fraction in the material, and the conversion at which the transition takes place can be calculated according to simplified Equation (13).

$$\frac{L_o}{\tau} = \frac{D_o}{L_o} \quad (13)$$

At this point all the parameters required to apply the RPM have been defined and determined, and the evolution of CaO conversion with time can be described by including them in Equations (4, 7, 13, 14 and 15). Expression (14) represents the evolution of CaO molar conversion for the kinetic controlled regime, and Expression (15) correspond to the evolution of CaO conversion with time for the regime that presents a combined control by the chemical reaction and the diffusion through the product layer.

$$\frac{L_o}{\tau} = \frac{D_o}{L_o} \quad \text{where } \tau \text{ is:} \quad (14)$$

$$\frac{L_o}{\tau} = \frac{D_o}{L_o} \quad (15)$$

Table 2 compiles the textural and structural parameters from the different materials tested and the kinetic parameters obtained through the fitting exercise that served to build the theoretical curves included in Figure 9 (shown as continuous lines).

Table 2. CaO:MgO sorbents: structural and intrinsic kinetic parameters for the carbonation reaction.

Molar ratio (CaO-MgO)	Particle size (mm)	L_o (cm/cm ³)	S_o (cm ² /cm ³)	ε	ψ	k_o (m ⁴ /Kmol -s)	E_{ak} (KJ/Kmol)	h_{k-d} (nm)	D_o (m ² /s)	E_{ad} (KJ/Kmol)	τ_p
2-1 CaO-MgO	< 100 μm	12.7*10 ¹³	13.3*10 ⁶	0.85	1.4	5.08±0.5* 10 ⁻⁶	1.34*10 ⁴	5	2.0*10 ⁻⁷	1.77*10 ⁵	
1-1 CaO-MgO	< 100 μm	8.8*10 ¹³	17.7*10 ⁶	0.74	0.88			25	2.0*10 ⁻⁵		
2-1 CaO-MgO	< 100 μm	5.9*10 ¹³	12.7*10 ⁶	0.75	1.14			60	2.58*10 ⁻⁵		
5-1 CaO-MgO	< 100 μm	6.7*10 ¹³	15.3*10 ⁶	0.76	0.84			80	7.58*10 ⁻⁵		

1	CaO-	< 100 μm	$13.2 \cdot 10^{13}$	$19 \cdot 10^6$	0.63	1.62	3.36 ± 0	$1.34 \cdot 10$	40	$9.0 \cdot 10^{-10}$	$9.43 \cdot 10^4$	
2							$.5 \cdot 10^{-6}$	4				
3	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$											
4												
5	5-1 CaO-MgO	0.6-1 mm	$1.3 \cdot 10^{14}$	$21.9 \cdot 10^6$	0.5	1.69	$5.08 \pm 0.5 \cdot 10^{-6}$	$1.34 \cdot 10^4$	40	$5.8 \cdot 10^{-4**}$	$1.77 \cdot 10^5$	3.5
6												
7	7-1 CaO-MgO	1-2 mm	$1.19 \cdot 10^{14}$	$21.4 \cdot 10^6$	0.51	1.60	$5.08 \pm 0.5 \cdot 10^{-6}$	$1.34 \cdot 10^4$	40	$5.8 \cdot 10^{-4**}$	$1.77 \cdot 10^5$	3.5
8												
9	CaO-	0.6-1 mm	$2.2 \cdot 10^{14}$	$30.0 \cdot 10^6$	0.49	1.63	$3.36 \pm 0.5 \cdot 10^{-6}$	$1.34 \cdot 10^4$	40	$5.8 \cdot 10^{-4}$	$1.77 \cdot 10^5$	3
10	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$											
11	CaO-	1-2 mm	$2.2 \cdot 10^{14}$	$29.1 \cdot 10^6$	0.49	1.74	$3.36 \pm 0.5 \cdot 10^{-6}$	$1.34 \cdot 10^4$	40	$2.8 \cdot 10^{-4}$	$1.77 \cdot 10^5$	3.2
12	$\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$											

A similar exercise has been performed with the material prepared $\text{CaO-Ca}_{12}\text{Al}_{14}\text{O}_{33}$ as inert support with a 90 % wt. CaO. The material structural and kinetic parameters obtained also included in Table 2. The kinetic parameters determined for both types of materials, fall in the range of values previously reported for the CaO carbonation reaction of natural sorbents, with a mean Activation Energy for the carbonation reaction kinetic constant of $(13.4 \pm 7.0) \cdot 10^3$ kJ/kmol, in close agreement with the values found by Sun et al. [71], $(29 \pm 4) \cdot 10^3$, Grasa et al. [66] $(20.3 \pm 1.0) \cdot 10^3$ kJ/kmol for natural sorbents, and recently reported by Zhou et al. (28.4 KJ/mol) [56] for a synthetic sorbent composed of 80 % wt. CaO and 20% wt. $\text{Ca}_9\text{Al}_6\text{O}_{18}$. The values were slightly lower than those obtained by the same authors through the OGM model (32.3 KJ/mol). This low activation energy, corroborates the low dependence that has shown the CaO conversion with temperature during the fast reaction regime.

The values for D_0 and E_{aD} are also compiled in Table 2, and the mean Activation Energy, E_{aD} (177 ± 10) $\cdot 10^3$ kJ/kmol, is in close agreement with the values reported by Bhatia and Pelmutter [65], compiled by Mess et al. [70] ($178 \cdot 10^3$ kJ/kmol for temperatures above 515 °C), reported by Grasa et al. [66] (163 ± 15) $\cdot 10^3$ kJ/kmol and slightly higher than the values reported by Zhou et al. [56] (88.7 kJ/mol) for the $\text{CaO-Ca}_9\text{Al}_6\text{O}_{18}$ material. The main differences appear within the pre-exponential diffusion coefficients, as the materials with lower CaO content required lower values to represent correctly the experimental values and ranged from $2.0 \cdot 10^{-7}$ m²/s to $7.58 \cdot 10^{-5}$ m²/s for the CaO:MgO 1:2 and CaO:MgO 5:1 materials respectively. This might indicate that the formation of the CaCO_3 layer, that it is intrinsically related with the diffusion coefficient, might be the parameter mostly affected by the type

of support or even the volume fraction of this support. In contrast, the intrinsic kinetic constant parameters for the reaction of CaO with CO₂ are hardly affected by the inert support nature or volume fraction (in the range inert fraction tested). These results are in agreement with the results presented by Liu et al. [55], and Zhou et al. [56] for sorbent materials with an 85% wt. CaO on to Ca₁₂Al₁₄O₃₃ and 80% wt. CaO on to Ca₉Al₆O₁₈ respectively.

Figure 9 shows some examples where the experimental data are represented together with model predictions. The figure shows how the model is able to predict the evolution of CaO conversion with time for the materials with different CaO content (CaO:MgO 1:2, 1:1, 2:1 and 5:1). As it can be observed the model is able to predict the CaO conversion with time fairly well, and it is able to model the transition between reaction rates. However there are discrepancies especially when sorbent approaches its maximum CaO conversion, (X_{carb}/X_{max} over 0.9), this is more evident in the tests performed at the highest temperatures and/or CO₂ partial pressure. Applying the arguments used to describe the transition between reaction regimes, it seems that there could be a second threshold on the CaCO₃ product layer, where the reaction regime is purely controlled by the diffusion coefficient, and where the chemical reaction no longer controls the carbonation of the materials [65, 69].

Finally a complete particle model has been built that considers the transport phenomena towards the interior of the particle pore network and incorporates the reaction rates according to the RPM described above. In this way the particles have been considered as spherical, and the general mass balance of a reactant diffusing to the interior of the particle can be described according to Equation (16) [72]:

$$\frac{dC}{dt} = \frac{1}{r^2} \frac{d}{dr} \left(r^2 D_e \frac{dC}{dr} \right) - (r)_s \quad (16)$$

Where C is the reactant gas concentration in the particle (mol/m³) that depends on the position in the particle, and time ($C=C(r,t)$); r is the particle radius (m); D_e is the effective gas diffusion coefficient (m²/s) and $(r)_s$ is the carbonation reaction rate expressed in (mol/m³s). The system has to fulfil the following initial and symmetry conditions:

$$\text{and } \text{---} \quad (17)$$

And also the boundary condition that affects the external mass transfer coefficient:

$$\text{---} \quad \text{for } r=R_o \text{ and } t \quad (18)$$

The mass transfer coefficient k_g (m/s) has been calculated from the following expression:

$$\text{---} \quad (19)$$

that incorporates the Sherwood non dimensional number (Sh), , where Re is the

non dimensional number of Reynolds --- and Sc is the Schmidt non-dimensional number:

$$\text{---} \quad (20)$$

$D_{\text{CO}_2\text{-air}}$ is the molecular diffusion coefficient (m^2/s)

$$\text{---} \quad (21)$$

To account for the gas diffusion in the pore network, the efficient gas diffusion coefficient has been calculated according to Eq. (22), where ε is particle porosity, D_g (m^2/s) calculated according to Eq. (23)

$$\text{---} \quad (22)$$

$$\text{---} \quad (23)$$

Where D_k is the Knudsen coefficient (m^2/s) [69] according to (24), T is reaction temperature (K) and M the CO_2 molecular weight (g/mol), and τ_p is the particle tortuosity (non dimensional) that refers to the non uniform paths in the particle pore network.

$$\text{---} \quad (24)$$

In this work τ_p has been considered as an adjustable parameter. The model that describes the evolution of particle conversion as function of the operation variables and particle textural properties uses the Gauss-Seidel method based on the Successive Overrelaxion Method (SOR) algorithm to calculate the CO_2 concentration profile towards the interior of the particle and calculates the CaO conversion (local reaction rate, during an increment of time) on a certain number of virtual nodes defined in the particle (the number of nodes have been optimized to obtain consistent results and optimize the calculus time). The model incorporates the main features observed during the study of the reaction on the materials in powder form. This is, the chemical reaction controls the reaction rate for conversions below $X_{\text{carbK-D}}$, and a combined control by the chemical reaction and diffusion through product layer of CaCO_3 takes place from this point and onwards. The model input parameters are: reaction temperature and CO_2 partial pressure, material textural and physical properties, the kinetic parameters for the carbonation reaction, the product layer diffusion kinetic parameters, the product layer thickness that sets the transition between regimes and materials tortuosity. The material textural properties S_N , L_N and ε be estimated from Hg porosimetry of the fresh calcined solids (that allows the estimation of S_o , L_o and ε) and the ratio $X_{\text{carbN}}/X_{\text{max}}$ according to the following expressions:

$$\text{---} \quad (25)$$

$$\text{---} \quad (26)$$

And the porosity has been considered invariable along conversion. The carbonation kinetic k_s and E_{Ak} , and E_{AD} have been taken from the intrinsic kinetic parameters determined from materials in powder form (compiled in Table 2). The product layer thickness $h_{\text{k-D}}$ has been estimated from the experimental data through Equation (13), and a consistent value of 40 nm has been found for the materials in particle form. This value was lower than that found for the same material in powder form. This might indicate that the agglomeration process that confers the textural properties of the material in particle form might have an effect especially on the parameters those are affected the most by them. Finally the pre-

exponential factor for the diffusion coefficient (D_o), and materials tortuosity (τ_p) have been set as adjustable parameters in the model fitting exercise as these could be the most material dependent parameters.

Figure 10 shows the sensitivity of the model to the tortuosity parameter. The model predictions are compared with an experimental CaO conversion curve determined for the material CaO-MgO 2:1 molar ratio in a particle size cut 0.6-1mm. Input parameters for the model: reaction temperature 650 °C and p_{CO_2} 10 kPa, k_s , E_{Ak} , D_o and E_{aD} (as for materials in powder form); L_o , S_o and ε according to Table 2, ($X_{carbN} / X_{max}=0.85$). According to modelling results, an increasing τ_p , difficulties the diffusion of CO_2 towards the interior of the particle, and therefore the prediction of the model under estimates material conversion during the initial fast reaction stage when introducing the kinetic parameters determined for the materials in powder form. In contrast low values of tortuosity over estimates the material conversion. The best fit with respect to the experimental data was obtained for the value of 3.5, as it is shown in the example of Figure 10 left). Figure 10 right) shows the CaO conversion curves for the material in the particle size cut 1-2 mm, and the model predictions show how the value of tortuosity of 3.5 is able to predict correctly the CO_2 concentration profile towards the interior of the particle independently of particle diameter and CO_2 partial pressure.

Figure 10. Left) Model sensitivity analysis based on materials tortuosity. Dotted line represents experimental results for the CaO:MgO material 0.6-1 mm particle size cut at 650 °C and 10 kPa CO_2 .

Right) CaO conversion curves for the CaO:MgO material 1-2 mm particle size cut, at 650°C at two different CO₂ partial pressures. Material tortuosity has been set as 3.5 in the model.

Figure 11 shows the sensitivity of the model towards the D_0 , which is the parameter that was the most affected by factors as CaO content in the material and that could also highly affected by the variation of material textural properties through the particle production process. In this way, the Figure shows for a fixed value of tortuosity (Left figure, τ_p has been set as 2.5, right figure τ_p has been set as 3.5), the effect that the parameter D_0 has on CaO conversion curves. As it can be seen according to model predictions, the value D_0 mainly affects the curvature of reaction regime under combined control. The optimum pair of values to fit the experimental curves obtained were τ_p 3.5, and D_0 0.000585 m²/s.

Figure 11. Model sensitivity analysis based on D_0 (m²/s). Dotted line represents experimental results for the CaO:MgO material 0.6-1 mm particle size cut at 650 °C and 10 kPa CO₂. Left) Tortuosity has been fixed at 2.5 in the model. Right) Tortuosity has been fixed at 3.5 in the model.

Figure 12 Left) shows how the model is able to predict the sorbent carbonation curves as function of reaction temperature (at a given value of CO₂ partial pressure, and particle size cut). As it happened for the theoretical conversion curves obtained for the materials in powder form, the model over estimates the conversion when materials conversion is over 0.95 X_{max} , indicating that the product layer is well developed and the combined control might not suitable anymore. This situation is more evident on the

experimental curves obtained at higher reaction temperature and/or higher CO₂ partial pressure as the reaction time set in the experiments is sufficiently long to allow the materials to reach their maximum CaO conversion.

Figure 12. Left) Carbonation conversion curves for CaO/MgO 2:1 material, particle size cut 0.6-1 mm, pCO₂, 10 kPa at 650 °C and 700 °C. Right) Carbonation conversion curves for CaO/MgO 2:1 material, pCO₂, 10 kPa at 650 °C and two particle size cuts. Model predictions are represented in solid lines, τ_p set as 3.5 in the model and D_o set as 0.000585 m²/s in the model.

As it has been found for the materials in powder form, the value D_o , together with the product layer thickness that set the transition between reaction regimes, are the parameters that are mostly affected by particle textural and physical properties. Still, a single pair of values was found to be suitable to fit the experimental data obtained for particles formed with the material CaO:MgO 2:1 in the particle size cuts of 0.6-1 mm and 1-2 mm.

Figure 13 shows an example of the quality of the fitting predicted by the reaction model for the material CaO-Ca₁₂Al₁₄O₃₃ in a particle size cut of 0.6-1 mm. The best fitting for the experimental data was obtained with τ_p of 3 and a D_o 0.000585 m²/s. A value of τ_p of 3.2 and D_o of 0.000285 m²/s was required to fit the experimental data for the bigger particle size of 1-2 mm tested. In both cases a h_{k-D} of 40 nm

product layer thickness was obtained from the textural parameters of the materials and the experimental data through Equation (13).

Figure 13. Carbonation conversion curves for CaO-Ca₁₂Al₁₄O₃₃ material, particle size cut 0.6-1 mm, pCO₂, 10 kPa at 650 °C and 700 °C., Model predictions are represented in solid lines, τ_p set as 3.0 in the model and D_o set as 0.000585 m²/s in the model.

Conclusions

In this work CaO-based CO₂ sorbents have been synthesised, characterised and tested. The effect of inert support and CaO content on materials chemical stability and reactivity has been determined. In this way materials with CaO contents between 40 % wt. to 90 % wt. on to MgO (synthetic dolomites) have been prepared following a co-precipitation route and materials with CaO contents between 60 % wt. and 95 % wt. have been prepared by mechanical mixing with Ca aluminate cement, followed by a calcination stage to form Ca₁₂Al₁₄O₃₃ as inert support. Some selected materials have been processed through an agglomeration process to produce sorbent particles within two different particle size cuts (0.6-1 mm and 1-2 mm) suitable for operation under fixed bed applications. The textural characterisation of the materials indicate that for the synthetic dolomites, and increment in the MgO content results in an increased BET surface area and a slightly increment in materials porosity. The pore size distributions show that materials with higher MgO content present a relevant fraction of pores in the

range of 10nm diameter. With respect to the materials prepared through mechanical mixing followed by calcination, increasing the Ca cement aluminate content resulted in materials with intermediate species apart than CaO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, and resulted in materials with lower BET surface area and also lower porosity, with bigger average pore size diameter. Materials CO_2 carrying capacity has been evaluated along multiple calcination/carbonation cycles in a TGA apparatus, and the results corroborate that a minimum amount of inert specie is required to maintain an improved with respect to only CaO containing materials. In this way, a minimum amount of 10 to 15 % wt. was required to maintain a stable and improved CO_2 carrying in the long term performance. The experimental results also corroborate that reducing the amount of CaO in the composition of the material diminishes the decay in CO_2 sorption capacity that typically presents CaO-based materials. Two materials have been selected to produce particles (0.6-1 mm and 1-2 mm particle size cuts) through an agglomeration process the CaO/MgO 1:2 molar ratio and the CaO- $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (90 % wt. CaO). These two materials have been compared in the long term performance and the synthetic dolomite presented higher CO_2 sorption residual capacity being able to capture up to 0.3 gr. CO_2 /gr. calcined material compared to the 0.2 gr. CO_2 /gr. calcined material that is able to capture the CaO- $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ material. The agglomeration process altered materials textural properties, and this was more dramatic for the synthetic dolomite as both BET surface and porosity were lower than for the materials in powder form. With respect to the kinetic study, experimental tests to the materials in powder form have been performed to determine the intrinsic kinetic parameters for the carbonation reaction of CaO. The sorbent carbonation conversion curves present similar characteristics to those obtained with natural CaO-based sorbents. The experimental results have been fitted to the RPM, and it has been observed that the CaO content and inert nature had very low influence on the carbonation kinetic constant k_s (or more precisely to k_o and E_{aK}) and on the activation energy correspondent to the product layer diffusion coefficient (E_{aD}), being the values obtained also very close to those determined for natural CaO-based sorbents. In contrast, CaO content, and/or inert specie had an important effect on the average product layer thickness that determined the transition between reaction rate regimes and also on the pre-exponential factor for the

product layer coefficient (D_o). Still, the RPM has been able to predict the evolution of CaO conversion with time as function of reaction temperature and CO_2 partial pressure. Once the intrinsic kinetic parameters have been determined, a complete particle model that is able to account for mass transfer phenomena through the pore network has been developed. The model that describes the evolution of particle conversion as function of the operation variables and particle textural properties uses the Gauss-Seidel method based on the SOR algorithm to calculate the CO_2 concentration profile towards the interior of the particle and calculates the CaO conversion on a certain number of virtual nodes defined in the particle (the number of nodes have been optimized to obtain consistent results and optimize the calculus time). The model has been proved to be valid to fit the experimental results and is able to predict sorbent carbonation conversion as function of temperature, CO_2 partial pressure, and particle size.

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NOTATION

a, b	stoichiometric coefficients for carbonation reaction
C	concentration of CO_2 (kmol/m^3); b bulk concentration; e equilibrium
D	effective product layer diffusivity (m^2/s)
D_o	pre-exponential factor in Equation (9) (m^2/s)
D_p	$bM_{\text{CaO}}DC/a_p$ apparent product layer diffusion (m^2/s)

$E_{a_{K,D}}$	Activation energy for the kinetic regime, K; and for the combined diffusion and kinetic regime, D, (kJ/kmol)
h_{K-D}	product layer thickness (m); K-D transition between reaction regimes
k_{so}	pre-exponential factor in Equation (8) ($m^4/kmols$)
k_s	rate constant for surface reaction ($m^4/kmols$)
$L_{o,N}$	initial total length of pore system (m/m^3); N pore length for cycle N
M_{CaO}	molecular weight of CaO (kg/kmol)
R_i	pore radius (m)
$S_{o,N}$	initial reaction surface (m^2/m^3); N reaction surface for cycle N
t	time (s)
$V^M_{CaO, CaCO_3}$	molar volumes ($m^3/kmol$)
X_{carb}	CaO molar conversion; N, relative to cycle N; K-D transition between reaction regimes; r residual CaO conversion
X_{max}	maximum CaO molar conversion according to their composition
Z	ratio volume fraction after and before reaction
<i>Greek Letter</i>	
α	Volume fraction of $CaCO_3$ invading a pore volume
β	$2k_s a p(1-\varepsilon)/M_{CaO} b D S_o$
δ	decrease in pore radius upon carbonation (m)

ε	porosity
$v_o(r)$	pore radii distribution
ρ	density kg CaO/m ³ material
τ	$k_s(C_b - C_e)S_o t / (1 - \varepsilon)$
Ψ	$4\pi L_o(1 - \varepsilon)/S_o^2$

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HIGHLIGHTS

- CaO-based sorbents have been produced on to MgO and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ inert supports
- The CaO content of the material determined its chemical stability
- Materials intrinsic kinetic parameters for the carbonation reaction have been determined
- Sorbent particles have been produced from materials in powder form
- A complete particle reaction model has been developed