Reactivity of calcined cement raw meals for carbonation

by

J. Plou*, I. Martinez, G. Grasa, R. Murillo

Instituto de Carboquímica, ICB-CSIC

M. Luesma Castán 4, 50018 Zaragoza, Spain

Telephone: +34 976 733 977

Fax: +34 976 733 318

e-mail: jplou@icb.csic.es

*corresponding author

ABSTRACT

In this work, the suitability of two raw meals from cement manufacture was evaluated for use as CO₂ sorbents. The evolution of their CO₂ carrying capacity for the initial cycles was determined as a function of calcination conditions, and the Random Pore Model was applied to determine the kinetic parameters of the materials for carbonation. It was observed that the CO₂ carrying capacity of the materials was totally dependent on reaction surface, which varies significantly with the calcination conditions (in terms of temperature and partial pressure of CO₂). The presence of species other than CaO affected material sorption capacity but had no bearing on reaction kinetics. The calcined raw meal was able to reach maximum conversion in the short reaction times typical of entrained flow reactors, and the dependence of the critical CaCO₃ product layer formed on CaO with reaction temperature was estimated.

Keywords: cement industry, CO₂ capture, carbonation, raw meal, calcium looping

Graphical abstract

The initial reaction rate of calcined raw meals do not depend on the surface area. This is shown in different material with different textural properties and their kinetics determination. Surface area determines the critical conversion X_{k-D} and the behaviour of the diffusional controlled reaction rate along the cycles.

1. INTRODUCTION

From the perspective of sustainability, major efforts are being made to reduce greenhouse gases (GHGs), including carbon dioxide. Industry is responsible for 7% of non-energy-related anthropogenic CO₂ emissions released into the atmosphere [1]. One of the sources is cement production, which accounts for 5% of total emissions into the atmosphere [2]. The demand for cement is expected to increase in the coming years [3], and therefore it is important to act in order to reduce CO₂ emissions in the production processes. Standard cement production comprises several stages. Firstly, a blend of limestone, silica, iron and alumina is crushed to a fine powder called raw meal ($d_p < 100 \mu\text{m}$). The raw meal is fed into a system of suspension preheaters consisting of a series of 4-stage cyclones. During this step, the energy released by the counter-flow of exhaust gases from the kiln raises the temperature of the solids to 800°C. The solid enters the calciner and the raw meal is decarbonised with the energy obtained from the hot air exhausted from the kiln and additional fuel combustion.. The flow of raw meal continues to a rotary kiln where it is heated by burning fuel. The powder achieves temperatures up to 1500 °C, producing hot cement. Due to the metastability of the aluminosilicates, the cement must be cooled quickly in order to retain these in the final product. During this process, CO₂ is released by calcination of the calcium carbonate and fuel combustion. Approximately 2/3 of the emissions are associated with raw meal calcination and are inherent to the process. Therefore, although several strategies have been proposed to reduce carbon emissions, such as more efficient use of fuel and the use of alternative fuels [4], only CO₂ capture and storage (CCS) would be capable of achieving the strict control of CO₂ emissions required.

The post-combustion calcium looping (CaL) process is one of the most promising technologies for CO₂ capture to have been developed at MW scale and has been

implemented in La Pereda integrated in a coal power plant (1.7 MW_{th}), and by TU-Darmstadt (1 MW_{th}), and ITRI, integrated in the Cement Taiwan Company plant (1.9 MW_{th}) [5–12]. This technology is based on the capacity of calcium-based sorbents to react with CO₂ from a gas stream in a carbonator reactor [13–17] and the calcination of the formed CaCO₃ to produce a concentrated CO₂ stream in an oxy-fired calciner. A number of works have identified possible synergies of CaL through simulation works or laboratory-scale studies: the use of CaO as regenerable CO₂ sorbent in the CaL unit ensures that additional chemical substances do not have to be used, as it is obtained from the same raw material used for clinker production; modifications to key units (rotary kiln and clinker cooler) in existing conventional plants are minimum and the energy required for regenerating the sorbent could be recovered in a steam cycle, which can compensate for the consumption of electricity required in the CaL process (i.e. O₂ production and CO₂ compression) [14,15,17–24]. There are two main approaches for integrating CaL systems into cement production plants: a tail-end CaL process configuration and the integration of the CaL in the pre-heating tower [25,26]. In the first option, the CaL reactors treat the gases at the exit of the clinker burning line and the CaL CO₂ capture unit follows the standard configuration comprising two circulating fluidised bed reactors. In this way, the CO₂ gas stream produced in the rotary kiln is directed to the carbonator reactor after passing through the pre-calciner and pre-heating tower from the cement process. The CaCO₃ formed in the carbonator is decomposed in the calciner operating in oxy-fuel mode, requiring the CaL unit an air separation unit. The purge from the CaL is further ground and mixed with additives to produce the raw meal. The most highly integrated option includes the use of raw meal as feedstock in the CaL system and operates with a heavy purge. Romano et al. [20] proposed feeding the finely ground raw meal directly into a suspension preheater in which hot gas and the cold solids come into contact

sequentially inside risers and are then separated in cyclones that heat the solids up to 650 °C. The preheated raw meal is sent to the oxy-fuel calciner at about 920 °C, in which the purge of calcined raw meal is high, around 55%, and then introduced directly into the rotary kiln. The rest of the sorbent is looped back into a certain part of the suspension preheater acting as a carbonator, capturing the CO₂ from the flue gas exiting the rotary kiln. One of the key points of the integrated process is that the heavy purge is necessary in order to feed the cement production process, causing the sorbent to undergo a small number of cycles. Moreover, a variation of this integrated scheme proposes the use of entrained flow reactors for the carbonation unit and has been studied in the work of De Lena et al. (Figure 1 represents a simplified scheme) [25,27]. Given the small particle size of the raw meal, which is classified as Geldart A powder (typical $d_p \sim 50 \mu\text{m}$) or Geldart C powder ($d_p < 20 \mu\text{m}$) [28], an entrained flow reactor is more suitable in contrast to the standard CaL applications in which the solid is transported into circulating fluidised beds (CFB), as the typical d_p is above 100 μm , corresponding to a Geldart B powder. The solid/gas ratio is low in entrained flow reactors in comparison with CFB reactors and the contact time is in the range of only a few seconds [29].

The use of raw meals as a CO₂ sorbent is a relatively recent concept, but it is an interesting alternative to evaluate with the aim of achieving zero emissions for cement manufacturing plants [14,19,20,22,23,30,31]. Raw meal is a mixture of fine powdered limestone, silica, alumina and iron oxide and only the CaO present in the limestone is able to act as the CO₂ sorbent. Few studies have analysed the behaviour of raw meal as a CO₂ sorbent in CaL systems; however, experimental results by Pathi et al. [22] show that as the limestone decays with the number of cycles, so does its carrying capacity. These authors reported a correlation between the raw meal BET surface area calcined under different conditions (temperature and CO₂ partial pressure) and the CO₂ carrying capacity of the material.

They concluded that, although new phases can be formed during the calcination of raw meal at high temperature and/or in the presence of CO₂, such as belite, sintering was the main reason for the reduced CO₂ carrying capacity. A recent work by Alonso et al. [32] analysed the effects that calcination conditions and the aggregation level of raw meal components had on their CO₂ carrying capacity, recommending an operation window for the calcination process in order to reduce the deactivation of raw meal as CO₂ sorbents.

During a standard cement manufacturing plant process, the raw meal is converted into clinker in two steps: calcination and clinkering. Calcination needs a temperature of 900 °C for decarbonisation to take place. Clinkering, the subsequent step, requires the temperature to be increased up to 1500 °C in order to generate various solid-solid reactions and produce diverse calcium silicates and aluminates. Dicalcium silicate, or belite, starts to form at a calcination temperature of 900 °C, and this has been proved to be inert for CO₂ capture [32,33]. Therefore, calcination conditions in the CaL process will determine the carrying capacity of the sorbent in relation to the amount of free CaO and the textural properties. In the works of Pathi et al. [22] and Alonso et al. [32], belite is detected (but not quantified) when the raw meal is calcined at temperatures over 900 °C and/or in presence of CO₂ and steam.

A critical aspect for the design of entrained flow reactors is the reactivity of the materials under relevant conditions for the process, which include short residence times and the existence of a temperature profile along the reaction path. Different expressions to describe the behaviour of the carbonation reactions of CaO-based materials have been proposed in the literature through the diverse solid-gas model [34–39]. The reaction consists of two stages: a fast stage followed by an extremely slow one. As the reaction depends heavily on surface area, a model based on the pore distribution was proposed by Sun et al. [38] in which the only fitted parameter is solid-state diffusivity, D_p , and where

pore distribution is taken as an initial value. Li et al. [37] proposed a model that calculates a CaCO_3 island distribution over the surface that depends on temperature and where the fitted parameters are the chemical reaction rate coefficient (k), surface diffusion coefficient (D_s) and island size distribution (N_e). The results were validated with an atomic force microscope (AFM) in which the islands were directly measured [40]. Stendardo et al. [41] describes the behaviour of carbonation with a shrinking core model applied to the particles and a diffusion coefficient that changes non-abruptly throughout the conversion of the particle. As conversion proceeds, the resistance to diffusion of the CO_2 through the layer increases and is represented by an exponential decay equation.. The random pore model (RPM) has been successfully used in several works [34–36,42,43] and the two stages are fully explained by intrinsic kinetic parameters. In this case, the pores are randomly distributed and related only to a structural parameter based on geometry. Variations of the RPM have been proposed in the literature to model the carbonation of CaO -based materials that have undergone multiple reaction cycles [34,44]. In order to apply these models, three main parameters are required with which to describe the evolution of CaO conversion: the intrinsic kinetic parameter (k_s), product layer diffusion coefficient (D) and the critical mean product layer (h_{k-D}). In the literature, the thickness of this layer is determined in a short range of carbonation temperatures ranging between 600°C and 700°C , and its value varies from 30 to 50 nm [34,39,42,45,46]. The dependency of the carbonation reaction with respect to crystallite size was studied by Biasin et al. [47]. Instead of a uniform product layer, a formation of “conically shaped product islands” was proposed with a size varying between 20 and 150 nm. Li et al. [37] developed a rate equation theory for the carbonation reaction, through which they described the growth of CaCO_3 islands as a function of temperature and that a higher carbonation temperature led to higher conversion during the fast reaction stage.

This work aimed to determine the parameters that mostly affect the reactivity of commercial raw meals for the carbonation of CaO, placing special emphasis on short reaction times and evaluating the reaction within a wide range of temperatures (450°C to 700°C) as the reactor was adiabatic in design, and therefore a distribution of temperatures could occur while the solids were fed in and flowed through the reactor. The experimental results were fitted with the previously used RPM, as the model describes the evolution of sorbent conversion with time [34]. Additionally, an expression that varies with temperature for the critical product layer was proposed. CO₂ carrying capacity was strongly affected by the textural properties (surface area and pore distribution) of the sorbent after calcination and the effect of temperature and reaction time was studied. The effect of other minor components (calcium silicates and aluminates) was studied through the determination of free CaO present in the sample.

2. EXPERIMENTAL SECTION

The experimental work presented in this work was devoted to determining the CO₂ carrying capacity and kinetic parameters for the CaO carbonation of raw meal materials with different textural properties and/or in presence of belite. Therefore, two different raw meals (RM-1 and RM-2) were calcined in a furnace under diverse conditions of temperature and reaction atmosphere to produce a sufficient amount of material for textural and structural characterization. Different analytical techniques were used to determine the textural properties of the calcined and fresh raw meals. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis was used to determine the elemental composition of the fresh samples. BET surface area was determined in a Micrometrics ASAP 2020 instrument according to the ISO 9277 standard. The BET

surface area is calculated from the physisorption of nitrogen up to a relative pressure of 0.3 and the accuracy of the instrument is 0.01 m²/g. The pore structure of the samples was determined by Hg porosimetry in a Micromeritics AutoPore V instrument according to the norm ISO 15901. Hg porosimetry is a method of intrusion of the non-wetting substance at high pressure in which the pore distribution is determined. The accuracy of the instrument is 0.04 mL of Hg. The true density of the samples was obtained by He pycnometry in a Micromeritics AccuPyc II and the method principle is the displacement of a known He volume by the material volume with an accuracy of 0.03% of the measured density. The particle diameter of the fresh samples was determined by laser diffraction using the Tornado Dry Powder Module of a Beckman Coulter LS13320 device according to ISO 13320. X-ray diffraction (XRD) analyses were carried out in a Bruker D8 Advanced diffractometer with an instrument alignment accuracy of 0.01° and according to the UNE-EN-13925 standard. The results were evaluated using specialist software (Diffrac.Suite from Bruker) in order to determine phase composition. Also, various mixtures were prepared containing different concentrations of sand and CaO and the areas under the peak with highest intensity for CaO and SiO₂ were calculated. A calibration curve representing area versus concentration was obtained and used for the determination of free CaO in the samples analysed in this work.

In order to determine the CO₂ carrying capacity and kinetic parameters of the materials, carbonation/calcination experiments were performed in a thermogravimetric analyser (TGA) designed for the CaL process. The TGA, previously described by Grasa et al. [34], comprised a two-zone furnace in which each zone was set at different temperature. A pneumatic piston moved the furnaces vertically, thus allowing the sample deposited in a handmade platinum sample pan to undergo alternating calcination and carbonation conditions. The reaction gases were regulated by mass flow controllers. In order to avoid

the effects of interparticle diffusion, 3 mg of raw meal was tested. Moreover, the total flow of the gases was $4.7 \times 10^{-6} \text{ m}^3/\text{s}$, making it possible to eliminate any effects of external diffusion. For the cyclic calcination/carbonation tests, the carbonation temperature was set at 650 °C, and a CO₂ partial pressure was set at 10 % vol. These operating conditions were selected based on the premise that the initial concentration of the CO₂ stream entering the carbonator unit would be 20%, according to the work of Campanari in the Cemcap project [48]. When 90 % CO₂ capture efficiencies are expected, the average concentration in the reactor could be considered as 10% vol. For kinetic parameter determination, the fresh raw meal was placed in the sample holder. Working temperatures were 900 °C for calcination and between 450 °C and 700 °C for the carbonation reaction.

3. RESULTS AND DISCUSSION

Two raw meals from two different cement manufacturers were characterized and tested. The material named RM-1 was a natural marl, and the solid named RM-2 was a commercial raw meal, mixed mechanically and consisting of clay, sand and limestone. According to the chemical analysis obtained by ICP (Table 1), both raw meals were observed to be similar in composition and highly resembling the raw meals for leading Portland cements [49,50]. As the raw meals were commercial samples, such similarities in composition were to be expected, as they comply with legal regulations (ASTM C150 [51] and EN 197 standards). The difference in the total percentage calculated was due to minority components not included in the chemical analysis. Among these components, gypsum (CaSO₄) usually appears in standard Portland cements. Additional qualitative analysis in XRD confirmed the presence of elemental sulphur and CaSO₄ in the samples, respectively. Particle size analysis of both materials revealed that the natural marl RM-1

presented an average particle size of 10.65 μm compared with the 48.86 μm presented by the raw meal prepared by grinding and mechanical mixing.

Table 1. Chemical composition of raw meals and some reference raw meal for Portland cement (PC).

Material:	RM-1	RM-2	PC,1 [49]	PC,2 [50]
CaO (%)	63.25	62.06	66.52	62-68
SiO ₂ (%)	19.51	20.26	21.24	21-24
Al ₂ O ₃ (%)	6.08	4.45	4.61	4-8
Fe ₂ O ₃ (%)	3.23	3.15	3.23	2-5
MgO (%)	0.96	1.46	2.27	---
K ₂ O (%)	1.37	1.22	0.42	---
TiO ₂ (%)	0.24	0.19	0.28	---
Na ₂ O (%)	0.32	0.04	0.35	---
Total (%)	94.96	92.83	98.92	---
LOI* (%)	34.75	34.83	---	---

* Loss on ignition

To evaluate the effect that calcination conditions had on the textural and structural properties of the raw meals, two samples of each were calcined in a tubular furnace at 900 °C for 1 hour: one sample in air, and the second sample in 50% vol. air/50% vol. CO₂. The materials were characterized by XRD diffractometry (Figure 2) in order to determine the existing crystalline phases and any new phase formed via reactions R.1–R.3. There are two competitive reaction paths for obtaining belite, hence reducing the amount of free CaO. The first of these is the direct solid-solid reaction R.1, while the other is the reaction in series R.2 and R.3. Carbonate has a lower melting point than CaO, and consequently R.1 is supposed to be faster than R.3. According to the spectra, the main phase was CaO, followed by SiO₂ with small amounts of belite (Ca₂SiO₄). The mass concentration of SiO₂ in both samples prior to calcination was very similar, but after calcination, the SiO₂ peak at 26.7 ° was lower in the RM-1 sample. In contrast, the peak at 41.2 ° corresponding to

Ca₂SiO₄ presented higher intensity in this sample. This indicates that the conversion to Ca₂SiO₄ was higher than for the RM-2 sample and it could have taken the form of reactions R.1 or R.3. The RM-1 powder had a smaller particle size than the RM-2 sample (Figure 3), so the solid-solid reaction between CaO and SiO₂ was better for the RM-1 sample as it presented a higher contact area.

R.1

R.2

R.3

BET analysis of the calcined materials showed a clearly lower surface area for the calcined RM-1 sample (3.6 m²/g) with respect to calcined RM-2 sample (6.6 m²/g), indicating that, despite the low amount of belite formed, the natural marl has been affected by the sintering phenomenon during the calcination.

Given the results of the textural analysis (lower BET surface area and higher belite formation), a lower CO₂ carrying capacity was expected for the natural marl. In order to corroborate this, fresh samples of both raw meals underwent calcination/carbonation cycles in the TGA described in the experimental section. The experimental conditions that served for comparison of the raw meal performance included calcination in air at 875 °C and carbonation in 10 % CO₂ vol. in air for 5 minutes at 650 °C.

Figure 3 represents the evolution of the CO₂ carrying capacity of the materials with the number of reaction cycles, expressed as mol CO₂ reacted/mol CaO in the material (according to ICP analysis). The decay observed was in agreement with the results published in the literature on cement raw meals [22,32]. The conversion presented by RM-1 was lower than 20% on coming out of the first cycle, and its CO₂ carrying capacity

decreased throughout the cycles. RM-2 sample conversion started from 60%, as can be seen in the inlet graph. In comparison with the theoretical evolution of the capture capacity found in the literature [13], RM-2 conversion is nearly 80% of the theoretical curve, whereas the RM-1 sample fits to 30% of the theoretical curve. Pathi et al. [22] studied the effect of different components in synthetic raw meals by mixing CaO with Al_2O_3 , SiO_2 or Fe_2O_3 and found that the CO_2 carrying capacity decreased on coming out of the first cycle in all cases. These authors attributed the decay in sorption capacity to the loss of surface area produced by the new phases formed between the main species and also to the sintering (as XRD revealed an increase in the CaO crystallite size owing to increasing calcination temperature and/or increasing CO_2 in the calcination atmosphere). According to these authors, the presence of other raw meal components, especially Al_2O_3 and Fe_2O_3 , also has a negative effect on the raw meal tendency to sinter. The deactivation observed in the CO_2 carrying capacity of the raw meals may have occurred for two main reasons: deactivation due to the reduction in reaction surface caused by a sintering phenomenon and/or deactivation due to the loss of active CaO for the carbonation reaction resulting from reaction with SiO_2 (R.1–R.3) or other components present in raw meal. The diffractogram in Figure 2 shows the formation of belite in both raw meals. Although the belite peaks are more intense for the RM-1 sample, it was not possible to quantitatively determine the amount of Ca_2SiO_4 in the samples. However, by applying the calibration described in the experimental section, it was possible to determine the percentage of free CaO present in both calcined samples. RM-1 was shown to have 31 wt% free CaO, while RM-2 had 41 wt% free CaO. This corroborates the higher formation of aluminosilicates (belite) for the RM-1 material. CaO crystallite sizes were determined in the samples RM-1 and RM-2 when calcined with only air (RM-1 and RM-2) and with CO_2 (RM-1 CO_2 and RM-2 CO_2). The use of CO_2 in the calcination increased the size in

RM-1 from 169.4 nm to 192.1 nm, and in the case of RM-2 from 124.8 nm to 142.4 nm. These figures corroborate the BET analysis and the higher sintering experienced by RM-1 in relation to RM-2 during calcination. The main differences between materials rely on the smaller average particle size of RM-1, a natural marl, and the slightly higher Al_2O_3 content in this material, which is known to favour the sintering of raw meals [22]. The main conclusion drawn from this part of the work is that the contribution of both factors is important to explain the decay in sorption capacity presented by the raw meals tested. From then on, the experimental work to determine the kinetic parameters for the carbonation reaction focused on the RM-2 material. Special attention was paid to materials in which belite formation took place, and therefore not all the CaO was available for reaction with CO_2 , and also materials with different textural properties.

To produce samples with different amounts of free CaO and also different textural properties, RM-2 was calcined at varying temperatures in a furnace. These samples were texturally characterized by means of Hg porosimetry and BET specific surface area analysis and they underwent carbonation tests in the TGA described in the experimental section (at 650 °C and 10 % CO_2). Figure 4 shows the textural characterization of RM-2 calcined at different temperatures, Figure 4 shows BET surface area and pore size distributions. As can be seen, BET surface area diminishes with increasing calcination temperature (from 11.8 m^2/g at 800 °C to 4.3 m^2/g at 900 °C). Hg porosimetry of the samples showed that pore structure of the materials is also affected by calcination conditions (as widely reported in the literature [43,52–54]).

Hg porosimetry of the samples also revealed changes in the pore size distribution (see Figure 4). The calcination of the material at 800 °C resulted in a mean pore diameter of 60 nm, and this increased to 130 nm for the material calcined at 900 °C, because of internal sintering due to the temperature. This phenomenon has been also described in the

literature [52]. The pore structure of the CaO sorbents tends to evolve with the increasing number of calcination/carbonation cycles. Typical CaO values from calcined limestone may vary in the order of tens of nm [34,39,52]. With synthetic sorbents, the pore structure of the materials may depend on the production method, and also, of course, on calcination conditions. By way of example, Zhou et al. [43] found a mean peak at 130 nm in synthetic sorbents composed of 20 wt% $\text{Ca}_9\text{Al}_6\text{O}_{18}$ and 80 wt% CaO. Liu et al. [53] and Gonzalez et al. [54] reported similar behaviour where the pores in fresh samples were greater than 100 nm; however, after reaction, pores in the range of 20–100 nm appears in synthetic sorbents of 15 wt% mayenite ($\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$) and 85 wt% CaO, and a sorbent containing 83 wt% CaO, 14 wt% MgO and 3 wt% $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, respectively. In general, the more aggressive the calcination conditions (in terms of calcination temperature and/or CO_2 partial pressure during calcination), the lower the BET surface area and the larger the average pore diameter.

The XRD diffractogram of the calcined samples are shown in the Figure 5. It is possible to observe that the amount of belite (inlet graph) is higher for the sample calcined at 900 °C and that the XRD data greatly coincide for the samples calcined below 850 °C. According to the calibration described previously, the values of free CaO do not vary noticeably for the samples calcined up to 875 °C, representing approximately 56-57 wt% with respect to the calcined sample. In contrast, a decrease is observed for the material calcined at the highest temperature (900 °C), this coincides with a slight increase in the belite peak detected by XRD. In this case, the calculated free CaO was quantified as 52.2 wt%. Despite the formation of belite, the intensity of the peak reveals that it is a minor phase. It can therefore be stated that, in this case, sintering was mainly responsible for the loss in carrying capacity and not the formation of belite, which decreases the total amount of free CaO.

To evaluate any effect of textural properties and the presence of belite on material reactivity, fresh raw meal samples calcined in the furnace at different temperatures (ranging from 800 °C to 900 °C) were subjected to a test consisting of 5 carbonation/calcination cycles at 650 °C and 10 % vol. CO₂ in the TGA described in the experimental section. Calcination in the subsequent cycles (2 to 5) was performed at 900 °C in air in the TGA in order to obtain significant belite formation, as this was relevant for the active CaO present in the raw meal.

Figure 6 (a) shows CaO molar conversion after 5 minutes of carbonation during every cycle. As can be seen in the Figure, the initial sintering (and higher belite formation) caused by calcination in the furnace has a significant effect on the CO₂ carrying capacity present the materials in the first and consecutive cycles. For example, the sample whose first calcination in the furnace was performed at 900 °C presents very low conversion on coming out of the first cycle, but its decline in activity is reduced as the number of reaction cycles increases. According to the XRD (Figure 5) and the data from Table 2, it presents the highest belite content and lowest percentage of free CaO. In contrast, the samples calcined at lower temperature in the tube furnace showed better performance during the first carbonation, but higher decay with the reaction cycles.

The experimental curves for the first carbonation (expressed in terms of mol CO₂/mol CaO in Figure 6 (b)) show the typical conversion curves that have been widely described in the literature for the reaction of CaO with CO₂, where the two well-known reaction stages [22,34,42,45,53,55–57] can be observed, due to control by the chemical reaction during the initial reaction stage, followed by a second, slower reaction stage governed by a combined control between the chemical reaction and CO₂ diffusion through the product layer formed [39,42,46]. Finally, there should be a third reaction stage where the product

layer thickness is well developed and the kinetic constant no longer affects the carbonation reaction rate [34–36,42,43,58,59].

As determined via XRD, the intensity of the characteristic peaks that reveal the presence of belite shows differences among the materials. As previously described, it was not possible to quantify this species, although its presence did not seem to have any effect on the reactivity of CaO with CO₂, given that the initial slope in the conversion curves shown in Figure 6 (b) strongly coincides with the samples calcined at different temperatures. This finding is in agreement with recent studies on the effect that the inert support had on carbonation kinetics of synthetic CaO-based sorbents [44]. Figure 6 (b) shows that the samples are able to achieve a 20 % conversion in the initial 10 seconds, and that the main difference between reaction curves is the conversion at which the transition between reaction stages takes place. This has been related to the formation of a product layer of CaCO₃ on the CaO surface.

To determine the kinetic parameters governing the carbonation reaction for cement raw meals, the model developed by Bhatia and Perlmutter [36] was applied. This model has been widely described in the literature [34–36,44]. Bhatia and Perlmutter developed a general expression (equation 1) for the rate of fluid-solid reactions that included diffusion effects [35,36,42,58]. This model has been successfully applied to different CaO-based sorbents [34,43,46,59,60].

$$\frac{1 - \frac{1 - \frac{\Psi}{\Psi_0}}{\frac{\Psi}{\Psi_0}}}{\frac{\Psi}{\Psi_0}} = \frac{1 - \frac{\Psi}{\Psi_0}}{\frac{\Psi}{\Psi_0}} \quad \text{Eq.1}$$

The RPM assumes a distribution of cylindrical pores defined by a unique parameter, Ψ . The value is obtained by applying Hg porosimetry to equations 2–5. S_0 corresponds to the initial surface area per unit of volume; L_0 is the initial total pore length and ε the

porosity. The value of the structural parameter (Table 2) is similar to the work by Grasa et al. [34].

$$\frac{1}{\Psi} = \frac{1}{\Psi_0} \left(1 - \frac{1}{\Psi_0} \right) \quad \text{Eq.2}$$

$$\frac{1}{\Psi} = \frac{1}{\Psi_0} \left(1 - \frac{1}{\Psi_0} \right) \quad \text{Eq.3}$$

$$\text{Eq.4}$$

$$\Psi = \frac{1}{\Psi_0} \left(1 - \frac{1}{\Psi_0} \right) \quad \text{Eq.5}$$

It is possible to simplify the general rate expression at low conversions in which the reaction is controlled by the chemical reaction. β is a modified Biot number and the value is negligible at the beginning of the reaction. Consequently, the resulting expression (equation 6) is used to derive the intrinsic kinetic constant k_s . After the critical product layer is formed and the reaction passes to the second regime, the Biot number changes to a higher value and the expression is simplified into equation 7. The value of the apparent product layer diffusion coefficient D_p is obtained using this expression. The effective diffusion coefficient is the result of applying equation 8.

$$\frac{1}{\Psi} = \frac{1}{\Psi_0} \left(1 - \frac{1}{\Psi_0} \right) \quad \text{Eq.6}$$

$$\frac{1}{\Psi} = \frac{1}{\Psi_0} \left(1 - \frac{1}{\Psi_0} \right) \quad \text{Eq.7}$$

$$\frac{1}{\Psi} = \frac{1}{\Psi_0} \left(1 - \frac{1}{\Psi_0} \right) \quad \text{Eq.8}$$

$$\frac{1}{\Psi} = \frac{1}{\Psi_0} \left(1 - \frac{1}{\Psi_0} \right) \quad \text{Eq.9}$$

As a first attempt, the initial reaction rate (equation 10), consistent with a RPM at conversion 0 [36], was applied to estimate the reaction rate experienced by the materials at the moment when there is no product layer.

$$\frac{1}{\Psi} = \frac{1}{\Psi_0} + \frac{\Psi}{\Psi_0^2} \quad \text{Eq. 10}$$

The values extracted from Figure 6 (b) are represented versus the reaction surface corresponding only to CaO (extracted from textural characterization of the samples and the molar volumes of CaO and sample) in Figure 7. As can be seen in the figure, the value of the initial reaction rate is between 0.025 and 0.03 (s⁻¹), close to the values reported in the literature for natural limestones [34,36]. These values are almost constant and it can be observed that there is no dependence on the initial reaction rate on the surface.

Experimental data from Figure 6 (b) was useful to determine the conversion level at which the transition between reaction regimes takes place (X_{k-D}) at 650 °C for materials presenting different textural properties. This is a key parameter with which to enable detailed modelling of the transition between control by the chemical reaction and the combined control by the chemical reaction and the CO₂ diffusion through the CaCO₃ product layer formed [34–36,44]. The existence of a critical product layer thickness (and consequently, the existence of X_{k-D}) was first proposed by Alvarez and Abanades [45], estimated at 50 nm for a variety of CaO from natural limestone through multiple calcination/carbonation cycles [39], and experimentally determined in a series of research projects dealing with the reaction of CaO-based materials with CO₂ [37,47,59]. It has been reported that product layer thickness is highly affected by the composition of the material and particle morphology [44] and also by the temperature and CO₂ partial pressure conditions at which the carbonation reaction takes place [59]. In this way, and indirectly from the measured conversion in Figure 6 (a) and the surface area, the product

layer thickness setting the transition between reaction regimes (h_{k-D}) can be calculated by means of equation 11 [34,39] for the RM-2 material tested in this work. The calculated product layer has been referred to as the reaction surface that would correspond to CaO, according to material composition (from ICP analysis and the density of the components, $v_{CaO}=63.88\%$ is the ratio of molar volume of CaO, referred to as the sample molar volume) [46], and a consistent value varying between 119 and 136 nm has been found (an average value of 127 nm is taken for later discussion). See Table 2 where the h_{k-D} values are calculated and the textural parameters of the materials are included.

Eq.11

Table 2. Textural and chemical properties of the calcined RM-2

T_{Calc} (°C)	S_0 (m^2/m^3) x 10^6	L_0 (m/m^3) x 10^{12}	ε (-)	Ψ (-)	$X_{k-D,exp}$ (mol CO ₂ /mol CaO)	h_{k-D} (nm)	Free CaO (%)
800	10.4	8.01	0.618	2.09	0.42	136	56.29
825	9.06	13.8	0.619	2.19	0.33	123	57.80
850	6.34	18.1	0.644	2.01	0.22	119	56.76
875	5.48	38.3	0.674	1.91	0.19	122	56.29
900	4.29	53.6	0.661	2.12	0.17	136	52.26
						$h_{k-D,mean}$ (nm)	
						127	

To derive the kinetic data, a wide range of temperatures was used in the carbonation tests. In this way, temperatures between 450 and 700 °C were selected, as described in the experimental section. Figure 8 (a) shows the evolution of CaO conversion for the first cycle and at different carbonation temperatures. In this series of tests, the calcination temperature was maintained at 900 °C, so the initial textural properties of the materials were identical. As many as 5 reaction cycles were performed for each test (Figure 8 (b)).

As can be seen in Figure 8 (a), all the curves present the two differentiated reaction stages as previously described, but it is important to highlight that the conversion level at which the transition between reaction regimes takes place is highly dependent on temperature. Also, this transition between reaction regimes is abrupt, especially at lower temperature, but with temperatures above 650 °C, the transition is smooth and control by chemical reaction and diffusion are in competition. At conditions close to equilibrium, the rates of nucleation and growth are fast and the limiting step is the surface reaction [37]. This surface reaction comprises CaO and CaCO₃ mobility over the surface and is a thermodynamic process in which the temperature favours the overall reaction rate [37]. The left-hand side term in equation 6 was represented vs time for each cycle in every experiment, and the individual values of kinetic constants were determined from the slope of the curves. These kinetic constants were represented in an Arrhenius form and the values of k_{so} and E_A were determined (included in Figure 9). From the experimental data, it was consistently observed at every temperature that carbonation in any cycle presented no differences in terms of the kinetic parameters determined. Moreover, it was possible to describe the evolution of CaO conversion during any cycle by taking into account the corresponding surface area at every cycle using equation 9 and the kinetic parameters k_s and D obtained in the fitting of the first cycle. The change in available surface at the beginning was very sensitive to sintering, so the material coming out of the second cycle was similar to highly cycled materials. In order to diminish the error at this point, a differential determination of S_N is preferable. Figure 8 (b) shows the experimental curves for consecutive cycles for the series performed at 650 °C. As can be seen, the main difference between the curves is the conversion level at which the transition between regimes takes place, and this is related to the progressive loss in reaction surface with the increasing number of carbonation/calcination cycles.

Figure 9 shows an Arrhenius plot of the k_s and D values obtained from equations 6 and 7, respectively. The surface area, $S_0 \cdot v_{CaO}$, used in the calculations at first cycle is $3.50 \times 10^6 \text{ m}^2 / \text{m}^3$ and was calculated from the Hg porosimetry and CaO volume ratio. This area is approximately one order below the values obtained in calcined limes [34], and the obtained value for the kinetic parameter k_s found at 650°C , ($0.37 \times 10^{-5} \text{ m}^4 / \text{kmol s}$), was also one order higher than the values reported by Grasa et al. [34] ($0.05 \times 10^{-5} \text{ m}^4 / \text{kmol s}$) and Bhatia and Perlmutter [36] ($0.06 \times 10^{-5} \text{ m}^4 / \text{kmol s}$). Despite these differences, as described a few paragraphs previously, the initial reaction rate estimated for the calcined raw meal was similar to those reported in the literature for CaO based sorbents and the initial delta conversion at 615°C was 0.037 s^{-1} in this work. Grasa et al. reported values of 0.032 s^{-1} and 0.033 s^{-1} in two limestones [34], and Bhatia and Perlmutter reported 0.041 s^{-1} [36] at 615°C . Lopez et al. obtained values in a range of 0.036 and 0.039 s^{-1} , for a fine powder of synthesized samples with CaO/MgO molar ratios ranging from 0.5 to 2. In all cases, despite the composition or the surface of the solid, the initial reaction rate was in close agreement. To account for this finding, the RPM equation was modified with the purpose of comparison and equation 12 was obtained from equation 1. Here, a kinetic parameter k_{CaO} that accounts for the product “ $k_s \cdot S_0 / (1 - \epsilon)$ ” was included. Finally, k_{CaO} had a mean value of $30 \text{ m}^3 / \text{kmol s}$ at 615°C . The Arrhenius plot of k_{CaO} is represented in Figure 9. The surface area, S_0 , determines the behaviour of the reaction through the critical conversion X_{k-D} and β in the combined control stage.

$$\frac{\frac{\Psi}{\Psi}}{\frac{\Psi}{\Psi}} \quad \text{Eq.12}$$

The activation energy for the carbonation reaction obtained in this range of temperatures, $(24.13 \pm 3.6) \times 10^3 \text{ kJ/kmol}$, was similar to the values obtained by Sun et al. [46] (29 kJ/mol for limestones and 24 kJ/mol for dolomite), Grasa et al. [34] (19 kJ/mol and 21 kJ/mol

for two different limestones) and Lopez et al. [44] (13.4 kJ/mol for synthetic CaO/MgO sorbents). Other authors reported zero activation energy, such as Chuant et al. [61], Bhatia and Perlmutter [42], Li et al. [37] and Biasin et al. [47]. Sun et al. [46] proposed that the differences in activation energy were due to material structural properties. In thermodynamic terms, the energy barrier to be broken through involves chemical energy and mechanical structure-related energy [46].

An Arrhenius plot was applied for the apparent diffusion coefficient D and the value of D at 650 °C, $5.1 \times 10^{-13} \text{ m}^2/\text{s}$, was two orders below that found by Grasa et al. [34], $2.0 \times 10^{-15} \text{ m}^2/\text{s}$ and $2.5 \times 10^{-15} \text{ m}^2/\text{s}$. According to Li et al. [37,40], the effective diffusion coefficient is divided into three terms: grain boundary diffusion (D_{GB}), lattice diffusion (D_L) and surface diffusion (D_S). The surface diffusion (D_S) controls the initial growth in the fast reaction stage. During the diffusion-controlled step, CO_2 goes through the defects in the CaCO_3 grain boundaries (D_{GB}) and through the product layer (D_L); the effective diffusion coefficient being a contribution of both diffusion coefficients ($D_{\text{eff}} = f \cdot D_{GB} + (1-f) \cdot D_L$). Therefore, both diffusion types control the growth of the CaCO_3 produced. In the case of limestones, CaO is spread over the surface homogeneously, but for raw meal, due to the presence of other minor compounds, this oxide is dispersed heterogeneously and the CaCO_3 layer produced might not be uniform. Hence, the number of defects over the reaction surface is higher for raw meal than limestones, thus increasing the value of the D_{GB} coefficient, which results in an increase in the effective diffusion coefficient. The energy activation, $63.8 \pm 8 \text{ kJ/mol}$, was very low compared to the work with limes, 163 kJ/mol [34] and 178 kJ/mol [60]. Bhatia and Perlmutter [42] found two regimes in which the activation energy changes from 88.9 kJ/mol to 179.2 kJ/mol at 515° C, and this lower value of the activation energy has also been found in electrical conduction experiments. The ion CO_3^{2-} is accepted as the mobile species, and with regard to raw meals, the defect

sites and vacancies where the ion could move is higher than in a limestone, due to inert components and impurities. Additionally, Zhou et al. [43] reported an activation energy of 88.7 kJ/mol for a synthetic sorbent composed of 80% CaO and 20% $\text{Ca}_9\text{Al}_6\text{O}_{18}$, citing the main cause to be the morphology and texture of the sorbent. As explained by Li et al. [37,40], the reaction rate in the second step is limited by the surface reaction and is dependent on the number of carbonate islands created over the CaO surface. Sun et al. [46] explained that the differences in activation energy between a dolomite and a limestone lay in the structure of the particle and the lower strain energy, because of more available space for the growth of the product. Linking both theories, the great difference in energy activation is caused by the voids in the surface of the other components that allow the growth of the carbonate in this zone.

Based on the experimental conversion curves from Figure 8, an effort was also made in this work to correlate the effect that carbonation temperature had on the product layer thickness that sets the onset of the combined controlled regime. The layer at every carbonation temperature was calculated by the equation 11 and the critical conversion was that found from the fitted curve extracted from the Figure 8. The values obtained in this work were plotted together with the values reported in the literature (Figure 10) [34,39,44,47,59]. As an example, an in depth study of the effect of temperature on the critical product layer was conducted in the work by Biasin et al. [47] using synchrotron XRD and the evolution of the crystallite size during the carbonation reaction. When comparing the results of the critical CaCO_3 crystallite size reported by Biasin et al. [47], the diameter of the crystallites were found to be similar to the calculated thickness of the layer. Intense research has been carried out to describe the morphology of the CaCO_3 layer under diverse conditions [37,40,42,46,47,62,63], but it is possible to assume that the layer is a row of crystallites, which is supported by the theory of the island distribution

over the surface [37,40]. Biasin et al. proposed a linear dependency of the size of CaCO_3 crystallite with respect to carbonation temperature. However, an Arrhenius expression is proposed in this work to explain the dependency on temperature. As the thickness of the layer depends on the chemical reaction and the surface reaction, the increase in size is thermodynamically justified because of the surface diffusion of the CaCO_3 . Despite the thickness of the CaCO_3 product, the diffusion of CO_2 through the layer is possible at high temperatures and the conversion is noticeable. Activation energy of 38.8 kJ/mol has been found to relate to the diffusion (Figure 10). The Grasa et al. and Abanades et al. studies [34,39] state that the critical layer thickness in limestone carbonations varies from 30–42 nm and 30–64 nm, respectively. In the work of Lopez, the critical layer thickness varies between 57 and 96 nm depending on the ratio of CaO/MgO [44] (values corrected according to CaO only surface). The differences in thickness, according to work by Li [37], could be associated with the initial size of the CaO crystallite, and this will depend on several factors: calcination conditions, material composition, morphology and sorbent synthesis.

Eq, 13

4. CONCLUSIONS

Two different raw meal materials were evaluated in this work as CO_2 sorbents. The CO_2 carrying capacity of the materials was determined by the surface area available for reaction. It was experimentally observed that the calcination conditions had a dramatic effect on textural properties and therefore on material performance. Moreover, the particle size of the raw meals played an important role, due to the reaction between the calcic components and the alumina or silica to form inert species. High temperatures and

the presence of CO₂ favoured this process and, consequently, the free CaO present in the sample diminished with the temperature. The kinetic parameters for the carbonation reaction of raw meals were determined and the RPM model was successfully applied to describe the evolution of CaO conversion over time for materials with different textural properties and in presence of belite. The kinetic parameters in the carbonation were determined at temperatures ranging from 450 °C to 700 °C. Although the raw meal was a mixture of calcium oxide, alumina and silica, the intrinsic kinetics in the initial stage agreed with the literature and therefore there was no observable effect of new phases formed. The activation energy of 24.13 kJ/mol was similar to that found by other authors. The activation energy at the stage in which the diffusion of gases through the product layer controls the rate presented a lower value (63.8 kJ/mol) with respect to data referring to CaO from natural limestones and dolomites. The critical product layer thickness formed, which sets the transition between reaction regimes, can be described with an Arrhenius equation with an activation energy of 38.8 kJ/mol.

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Nomenclature

C	CO ₂ concentration (kmol/m ³)
C _{eq}	CO ₂ concentration at equilibrium (kmol/m ³)

D	apparent product layer diffusivity (m^2/s)
D_p	effective product layer diffusivity (m^2/s)
h_{k-D}	product layer thickness in the transition between regimes (m)
k_{CaO}	simplified kinetic constant ($k_{\text{CaO}}=k_s \cdot S_0/(1-\varepsilon)$) ($\text{m}^3/\text{kmol s}$)
k_s	intrinsic kinetic constant ($\text{m}^4/\text{kmol s}$)
L_0	initial total length of pore (m/m^3)
S_0	initial specific surface area (m^2/m^3)
S_N	specific surface area at cycle N (m^2/m^3)
v_{CaO}	ratio volume fraction of CaO respect to the solid (-)
X	CaO conversion (-)
X_{k-D}	CaO conversion in the transition between regimes (-)
X_{max}	CaO maximum conversion at the end of cycle (-)
Z	ratio volume fraction after and before reaction (-)

Greek letters

β	modified Biot modulus in the random pore model (-)
ε	porosity (-)
Ψ	structural parameter (-)

Acronyms

CaL	Calcium Looping
CFB	Circulating fluidised bed
GHG	Greenhouse gases
RPM	Random pore model
TGA	Thermogravimetric analysis

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CAPTIONS

Figure 1. Conceptual scheme of the integrated configuration of CaL process into a cement plant.

Figure 2. XRD diffractogram of samples calcined at 900 °C in air and mixture of CO₂/air.

Figure 3. Conversion of raw meals during 7 cycles of calcination/carbonation. Calcination conditions: T_{calc}=875°C and pure air. Carbonation conditions: T_{carb}=650°C and 10% CO₂ in air.

Figure 4. Pore structure and specific surface area according to different calcination conditions.

Figure 5. XRD diffractogram of calcined samples at different temperatures.

Figure 6. (Left) Final conversion after 5 minutes of carbonation at every cycle of calcination/carbonation of the calcined sample. (Right) First carbonation after calcination in furnace without calcination in TG. Carbonation in the TGA at 650°C and 10% CO₂. Subsequent calcinations at 900 °C and 100% air.

Figure 7. Initial reaction rate according to the area obtained by Hg porosimetry.

Figure 8. (Left) First carbonation at different carbonation temperature in TG. (Right) Carbonation at 650°C at different number of cycle. (Calcination temperature = 900°C)

Figure 9. Arrhenius plot of k_s , k_{CaO} and D . Values of $k_{s,0}$, $k_{CaO,0}$, D_0 and respective activation energy are in the fitted equation.

Figure 10. Comparison of critical layer thickness (this work) and values from bibliography.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10