Investigation of CaO-CO₂ Reaction Kinetics by In-situ XRD Using Synchrotron Radiation

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Abstract

In this work, in-situ synchrotron radiation x-ray powder diffraction (SR-XRPD), performed at the Advanced Photon Source (APS) facilities of the Argonne National Laboratory, was applied to investigate the CaO-CO₂ reaction. A set of CO₂ absorption experiments were conducted in a high temperature reaction capillary with a controlled atmosphere (CO₂ partial pressure of 1 bar), in the temperature range between 450°C and 750°C using CaO based sorbents obtained by calcination of commercial calcium carbonate. The evolution of the crystalline phases during CO₂ uptake by the CaO solid sorbents was monitored for a carbonation time of 20 min as a function of the carbonation temperature and of the calcination conditions. The Rietveld refinement method was applied to estimate the calcium oxide conversion during the reaction progress and the average size of the initial (at the beginning of carbonation) calcium oxide crystallites. The measured average initial carbonation rate (in terms of conversion time derivative) of 0.280 s⁻¹ ($\pm$ 13.2% standard deviation) is significantly higher than the values obtained by thermo-gravimetric analysis and reported thus far in the literature. Additionally, a dependence of the conversion versus time curves on the initial calcium oxide crystallite size was observed and a linear relationship between the initial CaO crystallite size and the calcium oxide final conversion was identified.

Keywords

CO₂ capture, carbonation kinetics, crystallite size, in-situ x-ray powder diffraction, synchrotron radiation, CaO-based solid sorbents.

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1. Introduction

In recent years, interest in the global warming problem has been growing noticeably. The scientific community agrees that climate changes worldwide observed are related to greenhouse gas emissions from flue gases and other sources, most prominently to carbon dioxide emissions, which have increased rapidly due to technological and industrial development (IPCC, 2005, IPCC, 2007). The main industrial sector involved in CO₂ emissions is the power generation industry, in particular power plants based on fossil fuel combustion and coal gasification, that still account for about one third of all anthropogenic CO₂ emissions. To attenuate the rate and magnitude of climate change, mitigation policies and/or the development of new practices oriented to affordably and efficiently remove the CO₂ from industrial gas streams must be adopted (IPCC, 2007). Among carbon dioxide capture approaches applicable to existing large point sources of CO₂, a promising cost effective technology under investigation involves the utilization of calcium based solid sorbents and exploits the reaction of calcium oxide with CO₂ to form calcium carbonate under operating conditions not reachable with other Carbon Capture and Storage (CCS) technologies, such as amine-based and ionic liquid scrubbing systems or physical adsorbents like zeolites and metal organic frameworks (Figuerola et al. 2008, Wang et al., 2011, Yu et al., 2012). The technique is widely discussed in the literature and recently has been reviewed by several authors (Stanmore and Gilot, 2005, Blamey et al., 2010, Dean et al., 2011, Kierzkowska et al., 2013). The chemical reaction $\text{CaO}_{(s)} + \text{CO}_{2(g)} \leftrightarrow \text{CaCO}_{3(s)}$ is reversible and hence this technology is based on cyclic stages of carbonation and of calcination and offers a number of advantages including a high sorption capacity for CO₂ at high temperatures, a low cost of sorbent manufacturing and regeneration, and the abundance of its natural precursor. Even though attention has been paid in literature to the carbonation reaction and to its kinetics (Bathia and Perlmutter, 1983, Kyaw et al., 1996, Kyaw et al. 1998, Lee, 2004, Sun et al., 2008a, Grasa et al., 2009, Khoshandam et al., 2010, Li et al., 2012, Yu et al., 2012, Wu and Lan,

2012, Rouchon et al., 2013, Zhou et al., 2013), several aspects of the carbonation reaction are still not clearly understood.

Currently, it is accepted that the chemisorption of carbon dioxide in CaO particles proceeds as a non-catalytic gas-solid reaction by means of a number of steps. These stages typically include external mass transfer, inter-particle diffusion (in case the particles form a particle bed), intra-particle diffusion (CO₂ diffusion inside the pores), diffusion through the carbonate product layer, and surface chemical reaction. When the gas phase mass transfer resistances (external, inter-particle, intra-particle diffusion) can be neglected, the carbonation reaction is controlled by the surface chemical reaction and by the product layer diffusion, and is characterized by an initial very rapid reaction stage, reasonably governed by the filling of small pores, followed by a much slower step limited by the product layer diffusion (Bathia and Perlmutter, 1983, Kyaw et al., 1996, Kyaw et al., 1998, Sun et al., 2008a, Grasa et al., 2009).

A crucial aspect is the determination of the surface reaction kinetic parameters. In fact, high reaction rates during the carbon dioxide capture by CaO solid sorbents are required to design carbonator reactors of reasonable size, and hence the fast stage of carbonation is especially interesting because CaO solid sorbents can achieve high degrees of conversion with short residence times. The quality of the estimated surface reaction rate constants is determined by the accuracy of the experimental data, specifically of the conversion versus time curves. To the best of our knowledge, in all the contributions available in literature investigating the intrinsic kinetics of the carbonation reaction the thermo-gravimetric approach was used to measure the conversion versus time curves (Bathia and Perlmutter, 1983, Kyaw et al., 1996, Kyaw et al., 1998, Sun et al., 2008a, Grasa et al., 2009, Wu and Lan, 2012). A typical value of the initial and/or maximum reaction rate (in terms of conversion rate at 615°C, with a CO₂ partial pressure equal to 10 kPa or higher) obtained through thermo-gravimetric measurements is 0.054 s⁻¹ (Sun et al., 2008a); similar values were obtained by Bathia and Perlmutter (1983). However, it is known that thermo-gravimetric measurements can be affected by gas phase mass transfer limitations (external, inter-particle and

intra-particle diffusion), especially for fast reactions such as the carbonation reaction (Ollero et al., 2002, Gomez-Barea et al., 2005, Song et al., 2006). Usually such resistances are reduced by increasing the gas flow rate (external diffusion), decreasing the thickness of the particle bed (inter-particle diffusion), and decreasing the particle size (intra-particle diffusion). While the inter-particle mass diffusion can theoretically be minimized by reducing the particle bed down to a monolayer, it is questionable whether the external mass diffusion is negligible in the available carbonation reaction thermo-gravimetric data. In fact, even though a few authors (Sun et al., 2008a, Grasa et al., 2009) claimed that their TGA experimental results are independent of the gas flow rate (using high flow rates), the resulting conversion versus time curves and the reaction rates can still be dependent on the external diffusion. This could happen if, even at high gas flow rates, the local velocities around/inside the TGA crucible (close to the sorbent particles) are low and do not change significantly with the gas flow rate, and the high mole (CO_2) consumption rate due to the surface reaction is still limited by the external diffusion. Measurement techniques alternative to the TGA could be therefore considered to provide CaO conversion versus time data (and reaction rates) not limited by the external mass diffusion and to check the validity of the available thermo-gravimetric data.

Another relevant aspect is the dependence of the carbonation reaction on the sorbent structural properties. Thus far, many contributions have focused attention on the impact of porosity, specific surface area and the structural parameter or on the impact of the pore size distribution on the carbonation reaction and its kinetics, by using different versions of the random pore/grain models (Bathia and Perlmutter, 1983, Sun et al., 2008b, Grasa et al., 2009, Khoshandan et al., 2010, Yu et al., 2012, Zhou et al., 2013). Instead, the impact of the calcium oxide/carbonate crystallite size on the sorbent performances are pieces of information not available in the literature when referring to the carbonation reaction with CaO-based solid sorbents. Molinder et al. (2012) recently used x-ray diffraction to measure the crystallite size of partially hydrated CaO sorbents in a study on simultaneous hydration and carbonation of CaO, partially hydrated CaO and of $\text{Ca}(\text{OH})_2$. However,

to the best of our knowledge, the dependence of the carbonation kinetics on the calcium oxide/carbonate crystallite size has never been investigated.

In this work the CaO-CO_2 reaction is studied by in-situ x-ray diffraction using synchrotron radiation. The in-situ x-ray diffraction technique provides an alternative method to the thermogravimetric analysis by which chemical changes affecting a sample can be monitored in real time while the material is subjected to external variables, including temperature and/or a reactive atmosphere, following the crystalline structural evolution of the species present in the system (Denys et al., 2009, Babé et al., 2012). Time-resolved x-ray powder diffraction using synchrotron radiation (SR XRPD) was applied to investigate the kinetics of the chemical transformations and the microstructural evolution of the samples during the CO_2 absorption process, in order to identify relationships between the calcium oxide conversion and the calcium oxide average crystallite size. Synchrotron radiation, which is characterized by a high brilliance, was chosen because it produces x-ray data with excellent accuracy and a high time resolution that are essential to investigate a rapid reaction such as the first stage of calcium oxide carbonation. Using such a technique, it was possible to obtain new kinetic data (namely, conversion versus time curves) under operational conditions not limited by the external mass transfer, thus representing the intrinsic kinetics of the carbonation reaction.

2. Experimental details

2.1 Materials used

The starting material used for all the experiments was commercial calcium carbonate purchased by AppliChem as marble granular (A6297) with a declared chemical purity higher than 99% (verified through x-ray diffraction analysis as well) and a particle size distribution varying between few microns up to 300 μm . Although particles were polycrystalline and their size would not have affected the diffraction significantly, the material was previously sieved to collect a fraction of powder with a controlled average particle diameter in the range of 150-160 μm . This size was

selected to ensure both a low compaction of the material within the capillary used for conducting in-situ x-ray powder diffraction experiments, and a minimal graininess in the 2-D diffraction raw images recorded. The minimal graininess of the 2-D diffraction images is an indication that the samples initially loaded in the capillary are characterized by a nearly ideal random distribution of the coherently scattering CaCO_3 crystalline domains (namely, by the absence of initial preferred orientations) and confirms the quality of the diffraction data.

2.2 In-situ SR-XRD experiments

The in-situ SR-XRPD investigation of the CaO-CO_2 reaction was performed at the beamline 17-BM-B of the Advanced Photon Source (APS), at Argonne National Laboratory. The experiments consisted of monitoring x-ray powder diffraction data during a single cycle of calcination and carbonation stages such that initial CaCO_3 samples were first thermally decomposed to obtain porous CaO , afterwards subjected to the carbon dioxide absorption process. The measurements were carried out using a versatile set-up especially designed for conducting in-situ x-ray diffraction studies in non-ambient environments (Chupas et al., 2008). The system is based on a flow cell/furnace that allows the control of several environmental parameters including temperature (up to 900°C) and atmosphere/gas flow conditions.

A small amount of sample (about 5 mg) was loaded into a 1 mm quartz glass capillary (0.1 mm wall thickness, 75 mm long), filling approximately 3-5 mm of the capillary. The capillary was arranged upon the flow cell system, in turn mounted on the instrument using a standard goniometer head. Through a set of tubes and fittings, the gas was forced to flow into the capillary, through the sample particles. In order to prevent any change in the position of the powder during the experiments, mainly due to the gas flow, the sample inside the capillary was stabilized by means of quartz wool positioned nearby the powder, at both capillary extremities. Heating was provided by two resistive elements placed immediately above and below the sample capillary. A K-type thermocouple, placed within the capillary in close proximity to the powder, was used both for sample temperature monitoring and control.

Experimental data were collected using an amorphous silicon-based flat plate detector from Perkin-Elmer (model XRD 1621 CN3-EHS, detector size of 2048x2048 pixels, pixel size of 200x200 μm). The wavelength ($\lambda = 0.72959(3)$ Å with a focused beam of 300 μm) and the sample-to-detector distance ($d = 450$ mm, giving a usable range of 2θ of 1-43°) were calibrated using LaB_6 as a reference material. Because the CaO-CO_2 reaction is typically characterized by a very rapid initial reaction period, followed by a much slower second stage, the collection of the diffraction data during the carbonation stage was performed for a total time of only 20 min and, in order to obtain results with a time scale suitable for kinetics studies, data were recorded continuously using a frame rate of 0.25 s per frame for the first 5 min of the reaction (i.e. 1200 patterns), followed by a frame rate of 1 s per frame for the next 15 min (i.e. 900 patterns). The raw images were reduced to one-dimensional diffraction patterns by means of FIT-2D software (Hammersley et al., 1996, Hammersley, 1997). Finally, the data were analyzed by the Rietveld profile refinement method using the General Structure Analysis System (GSAS) software (Larson and Von Dreele, 2004). In particular, the sequential profile refinement approach was used to process consecutive analyses (time-resolved measurements) and hence to collect results as a function of the carbonation time.

2.2.1 Preparation of the CaO samples and carbonation tests

Calcium carbonate is typically utilized as precursor for producing CaO sorbents through stages of thermal decomposition: calcination of initially non-porous CaCO_3 particles leads to CaO with a high porosity (theoretical free volume of pores up to 54%) thanks to the molar volume reduction (from 36.9 to 16.9 cm^3/mol) caused by the thermally induced CO_2 release. The resulting increase in specific surface area makes CaO particles more reactive towards the following CO_2 absorption stage. In this study calcium carbonate samples were first decomposed to investigate the CaO reactivity during the carbonation stage. Calcination stages were performed in N_2 atmosphere (at a pressure of 1 bar), with a flow rate of approximately 10 NmL/min and a heating rate of 10°C/min. The calcination temperature was varied in the range between 700°C and 900°C, while two different residence times at these maximum temperatures were selected, namely 5 min and 60 min. At a

defined calcination temperature, the time required to fully decompose a given amount of calcium carbonate decreases as the calcination temperature increases (Gallagher and Johnson, 1973, Borgwardt, 1985, Wilburn et al., 1991, Galan et al., 2013) and hence the operational conditions were chosen in order to ensure the complete decomposition of CaCO_3 samples, as well as to obtain fresh calcines with different average size of nascent CaO crystalline domains. Since it has been generally observed that the (local) CO_2 partial pressure markedly affects both the calcination rate (Gallagher and Johnson, 1976, Wilburn et al., 1991, Criado et al., 1995, Wang and Thomson, 1995a, 1995b, Galan et al., 2013) and the sintering process (Ewing et al., 1979, Beruto et al., 1984, Borgwardt, 1986, 1989a, 1989b, Mai and Edgar, 1989, Milne et al., 1990, Fuertes et al., 1991, Fierro et al., 2004, Manovic et al., 2009), N_2 flow within the capillary was used to facilitate the removal of the CO_2 released at the reaction zone during the calcium carbonate decomposition away from the solid surface, mainly to reduce its contribution on the sintering that can affect the sample during calcination stage at high temperature.

After the complete thermal decomposition of CaCO_3 , the new-formed CaO was cooled down (at $10^\circ\text{C}/\text{min}$, still keeping the sample under N_2) to the desired carbonation temperature. Afterwards, the carbonation stage was carried out isothermally at several temperatures between 450°C and 750°C . As mentioned, the overall carbonation time was set at 20 min for each of the tests. An atmosphere of pure CO_2 was used maintaining a constant flow rate of approximately $10 \text{ NmL}/\text{min}$ at a pressure of 1 bar. The transition between N_2 and CO_2 atmosphere was realized by means of an automatic switching valve.

2.3 Carbonation conversion and average crystallite size estimation

By means of the Rietveld profile refinement method, information about the structural changes of the sorbent samples, including CaCO_3/CaO phase and crystallite size evolution over time, as a function of both calcination conditions and carbonation temperature, were obtained. Calcium oxide mass fractions were estimated from the Rietveld quantitative phase analysis (QPA) of the diffraction data

refining phase scale factors (Larson and Von Dreele, 2004), and were used to calculate the CaO conversion $X(t)$ during the CO₂ absorption stages as:

$$X(t) = \frac{1 - w_{CaO}(t)}{1 - w_{CaO}(t) + w_{CaO}(t) \frac{MW_{CaCO_3}}{MW_{CaO}}} \quad (1)$$

where $w_{CaO}(t)$ is the calcium oxide mass fraction evaluated at consecutive diffraction analyses/scans (namely at a different time t) recorded during the experiments, while MW is the molecular weight of the species involved in the carbonation.

The average size of the CaCO₃/CaO crystallites in the material was also evaluated from the Rietveld refinements of the profile parameters. In particular, GSAS fits crystallite size broadening with the Lorentzian isotropic crystallite size-broadening factor (LX). The relationship between this (dimensionless) parameter and the average crystallite size (CS , in nm), for each crystalline phase within the material, was obtained by a rearrangement of the Scherrer's formula (Larson and Von Dreele, 2004):

$$CS = \frac{18 \times 10^3 K \lambda}{\pi LX} \quad (2)$$

where λ is the x-ray wavelength (0.07296 nm) and K is a dimensionless constant related to the crystallite shape taken as 0.9. During the refinements, only the Lorentzian size-broadening profile parameter was refined while the strain-broadening factor did not show a significant contribution. The Thompson-Cox-Hastings pseudo-Voigt-type function was used to fit the Lorentzian term and describe the peak shapes (Larson and Von Dreele, 2004). The temperature factors (Larson and Von Dreele, 2004) were adjusted to take into account the effect of the different carbonation temperatures on the crystalline structure evolution, namely the attenuation of the x-ray scattering caused by the thermal motion of the atoms within the crystal lattice (Dinnebier and Billinge, 2008, Als-Nielsen and McMorrow, 2011). A cosine Chebyshev function of 12 polynomial terms was applied to fit the

profile background. The structure models for the starting material (CaO) and the crystalline reaction product (CaCO₃) were taken from the literature; 261847-ICSD and 20179-ICSD were selected for lime and calcite respectively. The instrumental contribution to the line broadening was evaluated by refining the profile parameters for LaB₆. Finally, to achieve a careful control of the sequential refinement, in the analysis of the time-resolved patterns only the angular range of 10.5-31.5° of 2θ was used for the refinement of the global and the peak shape broadening parameters, as well as for the phase specific scale factors.

The quality of the fitting was then evaluated using the weighted residual factor (wRp) of the refined analysis of each diffraction pattern, in agreement with the method of the least squares used by GSAS as main refinement technique (Larson and Von Dreele, 2004). Good fittings for all the cases were obtained, with an average value of wRp of about 0.08 ($\pm 1\%$ of standard deviation) for the different time-resolved experiments performed. No preferred orientation corrections were required to obtain satisfactory fits of both CaCO₃ and CaO. A typical 1D-diffraction pattern and the related fit are shown in Figure 1.

3. Results and discussion

The data collected from the time-resolved measurements were used to calculate the profiles of the CaO conversion utilized for the reaction kinetics investigation, and of the calcium oxide average crystallite size trends during the CO₂ absorption process, in order to identify relationships between the carbonation rate/conversion and the structural properties of the crystalline species (CaO) involved in the reaction. Work is in progress to analyze the dependence of the carbonation kinetics on the calcium carbonate average crystallite size profiles over time, so that it has been excluded from the current study. A summary of all the experiments performed is reported in Table 1, underlining both the corresponding operating conditions and the main results obtained by Rietveld refinements for each test. As mentioned, in this work 20 min of carbonation was arbitrarily taken as reference time to estimate the final conversion for each experiment. The average size of the initial

CaO crystalline domains was calculated once each sample had reached the desired carbonation temperature (after the cooling down of the sorbent from the calcination conditions), and before switching the gas atmosphere from N₂ to CO₂ inside the capillary. The errors in the average crystallite size calculation were estimated from the standard deviation values provided by GSAS for the *LX* parameters, afterwards used in the crystallite size calculation.

3.1 Profiles of calcium oxide conversion

Curves of calcium oxide conversion (*X*) versus time (*t*) were obtained from the experiments performed at different carbonation temperatures, using CaO sorbents previously prepared through calcination stages carried out at several operating conditions. Two types of comparison were performed between the conversion profiles, namely i) as a function of the carbonation temperature, with CaO sorbent samples produced with the same calcination conditions (Figures 2-4) and, ii) at the same carbonation temperature, comparing the behavior of sorbent particles obtained from different calcination stages (Figures 5-7). In particular, different operating conditions during the thermal decomposition of calcium carbonate were selected to obtain fresh calcines with different average sizes of the CaO crystalline domains. In each of the Figures from 2 to 7 the complete conversion profile (up to 20 min of carbonation) is shown on the left side while a detailed view of the first instants of the reaction is plotted on the right side.

Conversion profiles as a function of the carbonation temperature were collected performing carbonation experiments with calcium oxide particles produced through three different calcination stages, namely at 900°C for 5 min (Figure 2), 900°C for 60 min (Figure 3) and at 700°C for 60 min (Figure 4). All the curves exhibit the characteristic shape of the carbonation reaction, including the fast initial reaction stage, up to a point/knee where there is an abrupt change in the carbonation rate that leads to the second slower stage (Bathia and Perlmutter, 1983, Kyaw et al., 1996, Kyaw et al., 1998, Sun et al., 2008a, Grasa et al., 2009). The first stage of the carbonation, occurring in the early instants of the reaction, was complete roughly after 5 s, showing reaction rates significantly higher than those typically observed in the literature (Bathia and Perlmutter, 1983, Kyaw et al., 1996,

Kyaw et al. 1998, Lee, 2004, Sun et al., 2008a, Grasa et al., 2009, Khoshandam et al., 2010, Li et al., 2012, Yu et al., 2012, Wu and Lan, 2012, Rouchon et al., 2013, Zhou et al., 2013). The second phase of carbonation is characterized by a plateau that was associated with the occurring of the product layer diffusion controlled regime. In most of the runs, it seems that a maximum extent of conversion was achieved after 20 min of reaction. However, in a few experiments (curves B and F in Figure 2, curves E and O in Figure 4) the conversion profiles still exhibit a slow increase in the CaO conversion trend after 20 min of carbonation. The majority of the profiles show final conversions above 50%, with the highest values around 70%, while only few experiments resulted in final conversions around 20% or below.

Even though at a CO₂ partial pressure of 1 bar, in the range between 450°C and 750°C, higher carbonation temperatures generally lead to higher calcium oxide conversions at a given carbonation time (Kyaw et al., 1996), according to these profiles the carbonation temperature apparently does not affect the value of the final conversions in the expected way. Experiments carried out at 450°C showed final conversions of approximately 60% (curves A and D in Figure 2 and Figure 4 respectively), which were higher than those observed at a carbonation temperature of 500°C (curves F and O in Figure 2 and Figure 4 respectively), 550°C (curves B and E in Figure 2 and Figure 4 respectively) and 750°C (curve G in Figure 2), as well as in the carbonation test performed at 550°C (curve M in Figure 3) a final conversion higher than that one measured for the corresponding experiment at 650°C (curve H) was observed. These unexpected trends of the final conversion as a function of the carbonation temperature indicate that other aspects may affect the CaO-CO₂ reaction. In particular, it can be noted that the majority of the sorbent samples produced with the same calcination conditions show large differences in the values of the initial CaO average crystallite size (see Table 1). To emphasize the effect of the calcium oxide initial (measured at the beginning of the CO₂ absorption process) average crystallite size on the reaction kinetics, conversion profiles for isothermal carbonations performed at temperatures of 650, 550 and 450°C were compared, as shown in Figures 5, 6 and 7 respectively. At a carbonation temperature of 650°C

(Figure 5), CaO sorbents with an initial average crystallite size of about 30 nm (curves C, K and L) achieved conversions of approximately 70% after 20 min of reaction, clearly higher than that ones obtained with sorbent samples characterized by an initial average size of their crystalline domains of about 50 nm (about 60%, curve J) and 250 nm (about 40%, curve H). A similar trend was observed for carbonation temperatures of 550°C (Figure 6) and 450°C (Figure 7) where particles with crystalline domains of about 40 nm (curves M, D and A) were converted to values higher than those achieved by sorbent samples with average crystallite sizes of 100 (curve B) and 124 nm (curve I) respectively.

Therefore, the conversion profiles point out that generally calcium oxide sorbents with a lower average crystallite size at the beginning of the carbonation reaction show a higher CO₂ capture capacity. In this way, the apparently unexpected dependence of the conversion profiles on the carbonation temperature (Figure 2, 3 and 4) can be explained: even though the sample are produced with the same (macroscopically) operating conditions during calcination, the particle properties (particularly the CaO crystallite size) are different and, therefore, in each of the Figures from 2 to 4 both the carbonation temperatures and the particle properties are different among different runs. In conclusion, for each of the Figures from 2 to 4, a straightforward comparison among different profiles as a function of only the carbonation temperature cannot be performed.

The reason why at the same (macroscopically) calcination conditions sorbent particles with different calcium oxide crystallite size were produced still needs to be explained. It should be reminded that the diffraction data used to build the conversion profiles of the CaO based sorbent samples reflect the behavior of only a small volume of the powder loaded inside the capillary. Because the size of the x-ray beam was about 300 μm and the internal diameter of the capillary was 1 mm, each conversion profile represents the CO₂ capture performance of a volume of less than 0.07 mm³. Assuming that the 150 μm calcium carbonate particles are spherical, the number of particles inside the volume spanned by the x-ray beam was small, namely of the order of 10-30 particles. Additionally, even though each sample was loaded inside the capillary with the same

procedure, it is notable that the compaction of the particles was not verifiable and it is likely that it was different among all the experiments performed. Therefore, it can be hypothesized that even with the same (macroscopically) calcination conditions and the same compaction procedure, the local (specifically, in the volume spanned by the x-ray beam) compaction extent could be different, thus determining different local fluid dynamic conditions, carbon dioxide concentrations and ultimately different local calcination conditions. Moreover, it can be reasonably assumed that sintering processes, favored at high temperature, occurred during the thermal decomposition of the calcium carbonate samples inducing alterations of the characteristic porous structure and of the crystallite size of the fresh CaO particles afterwards used for the carbonation experiments (Borgwardt, 1986, 1989a, 1989b, Mai and Edgar, 1989, Sun et al., 2007, Zhu et al., 2011). Specifically, it can be hypothesized that sintering phenomena took place at different extents among the different runs (even in those carried out with identical macroscopically operating conditions during the calcination) because of the in-homogenous local calcination conditions, determining morphological differences in the produced CaO calcines, especially in terms of crystallite size, as well as in terms of specific surface area and porosity.

Finally, it has to be specified that the change in the conversion accuracy, that can be observed in each profile in the Figures from 2 to 7 after the first 5 minutes of carbonation, reflects the change of exposure time applied during the collection of the x-ray data. As mentioned in Section 2, data were recorded continuously with a frame rate of 0.25 s per frame during the first 5 min of the reaction such that the first 1200 diffraction patterns arise from the data measured with an exposure time of the same duration of the frame rate, namely 0.25 s. After that, during the remaining 15 min of carbonation, the frame rate was increased to 1 s resulting in a longer exposure time (namely, 1 s) for each frame that determines the higher accuracy of the last 900 scans.

3.2 Effect of the initial CaO average crystallite size on the carbonation reaction

The comparison of the different values measured for the initial average crystallite size of the CaO based sorbents and the corresponding final conversions obtained for each experiment (summarized

in Table 1) points out an interesting result. The values of the final conversion are plotted in Figure 8 as a function of the initial CaO average crystallite size. Focusing on the runs in which the conversion was not significantly increasing after 20 min of carbonation (black circles in Figure 8), it can be observed that the lower is the initial average crystallite size of the new-formed calcium oxide, the higher the conversion of the sorbent particles evaluated at the end of the absorption experiments. A linear fitting of such experimental data provides the following relationship (solid line in Figure 8):

$$X_{\max} = -11 \times 10^{-4} CS_{CaO} + 0.705 \quad (3)$$

where $X_{\max}$ is the final (maximum) CaO conversion (obtained after 20 min of carbonation) and CS_{CaO} is the average size (in nm) of the CaO crystalline domains measured at the beginning of the carbonation reaction. This correlation is independent from the carbonation temperature maintained during each run, as well as from the operating conditions used to produce the initial CaO sorbent particles. It should be noted that the red crosses in Figure 8 represent the conversions measured after 20 min of carbonation in those experiments in which the conversion profiles were still increasing at the end of the carbonation. Since the reactions were evidently incomplete, the final conversions evaluated in these runs were not considered as accurate values for the maximum conversion potentially achievable from the sorbent particles.

The maximum CaO conversion ($X_{\max}$) can be estimated from the initial sorbent porosity through the following relationship (Sun et al., 2007):

$$X_{\max} = \frac{\varepsilon_0}{\left(\frac{1}{Z} - 1\right)(1 - \varepsilon_0)} \quad (4)$$

where ε_0 is the initial sample porosity available for the carbonation and Z is the molar volume ratio of calcium oxide to calcium carbonate that is equal to 0.46. Equation (4) is obtained assuming that the porosity is zero when the maximum conversion is reached. According to equation (4) different

maximum conversions at the end of carbonation can be obtained as a function of the initial sorbent porosity, which depends on the high temperature thermal treatment carried out during the preliminary calcination stage. However, it is reasonable to assume that the average value of the CaO initial crystallite size could reflect the morphological properties (specifically, the porosity) characterizing the sorbents at the beginning of the carbonation.

Rearranging equation (4), the initial porosity of the solid sorbents can be directly related to the maximum conversion reachable:

$$\varepsilon_0 = \frac{X_{\max} \left(\frac{1}{Z} - 1 \right)}{\left[1 + X_{\max} \left(\frac{1}{Z} - 1 \right) \right]} \quad (5)$$

Using equation (5), an estimate of the initial porosity of the CaO sorbent samples in each carbonation experiment was performed, and then correlated with the corresponding values of the average crystallite size of calcium oxide at the beginning of the CO₂ absorption processes, as shown in Figure 9.

The relationship, highlighted by the solid line in Figure 9, has been formalized through a linear fitting of the data calculated, leading to the following expression:

$$\varepsilon_0 = -4.707 \times 10^{-4} CS_{CaO} + 0.456 \quad (6)$$

As previously mentioned, because the evaluation of the initial porosity requires to consider only the maximum conversion physically attainable, those experiments that had not reached clearly a reasonable value of the maximum conversion at the end of the carbonation experiments (red crosses in Figures 8 and 9) were omitted from the calculation of the correlation reported. The trends emerging from Figures 8 and 9 suggest that sorbent samples with a smaller size of CaO crystalline domains at the beginning of the carbonation should have a higher initial porosity and hence more

pore volume available for the calcium carbonate growth that consequently leads to a higher final carbonation conversion.

3.3 Intrinsic reaction rate in the first carbonation stage

In addition to the determination of the average sizes of the CaO crystalline domains that characterize the solid sorbents at the beginning of the carbonation reaction, the in-situ x-ray powder diffraction analysis permitted a detailed analysis of the rapid first stage of the CaO-CO₂ reaction providing remarkable results about the carbonation rates.

The reaction rate of the calcium oxide carbonation is usually defined as a specific rate, namely as the CaO conversion time derivative dX/dt divided by $1-X$. Typically, the conversion time derivative at time zero (beginning of carbonation) is used in order to compare rates from different experiments. In particular, in the initial part of the first rapid stage of the carbonation reaction (at low conversions), the measured conversion rates are representative of the intrinsic reaction rate due to the surface chemical reaction because the product layer diffusion can be reasonably neglected. The conversion time derivative at time zero is equal to the maximum time derivative in grain models (Sun et al., 2008a) and in random pore models (Bathia and Perlmutter, 1983) in the regime controlled by the chemical kinetics when the structural parameter is smaller than 2 (such value is within the typical range for CaO based sorbents). Therefore, the estimate of the initial conversion time derivative characterizing the first stage of the carbonation reaction was performed in two ways, namely i) considering the maximum values of dX/dt for each CaO conversion profile, and ii) selecting a portion of the initial fast stage where the experimental curves of conversion versus time could be fitted through a linear relationship. In the former case, the values of CaO conversion at which the maximum conversion rates were computed were always lower than 0.2 (and always within the first second of reaction). In the latter case, for each run the experimental points used in the linear fitting were selected considering the data below both 25% and 50% of the corresponding final conversions, as shown for example in Figure 9, starting from the first non-zero value of the conversion.

The carbonation reaction during the fast reaction stage is frequently interpreted as controlled by the (intrinsic) surface chemical reaction (Bathia and Perlmutter, 1983). Accordingly, the effects of the product layer diffusion are neglected. However, other authors claimed that it is more reasonable to assume a regime of simultaneous chemical kinetics and product layer diffusion even during the first stage of carbonation, then followed by a pure diffusion controlled regime after that the product layer of CaCO_3 has reached a critical value (Sun et al., 2008a, 2008b, Khoshandam et al., 2010). Therefore, only at low values of CaO conversion it is correct to assume that the diffusional effects through the product layer of CaCO_3 are negligible. Therefore, the computed initial conversion time derivatives could underestimate the true values, because they could be partially affected by some product layer diffusion effects.

Despite that, both the approaches applied here to estimate the initial conversion rates underline a significant difference with the data reported in the literature. A summary of the calculated conversion time derivatives is reported in Table 2 (the estimate of the conversion rate using the linear fitting up to 50% of the final CaO conversion was not possible for carbonation profiles with final conversion lower than approximately 20%, namely for runs B, F, I and O). Even though the results in Table 2 show values of standard deviations between 9.6% and 13.2%, the carbonation rates observed during the first stage of each carbonation experiment are unequivocally a noteworthy result. In fact, such high conversion rates, with average values of the conversion time derivative between 0.280 s^{-1} and 0.239 s^{-1} , have never been previously measured for the CO_2 carbonation using CaO based solid sorbents. Typical values of about 0.05 s^{-1} reported so far in the literature by several authors are far from the values measured in this study: as mentioned, Sun et al. (2008a) estimated an initial maximum reaction rate of 0.054 s^{-1} at 615°C with CO_2 partial pressure equal or higher to 10 kPa. A corresponding similar value was obtained from the data of Bathia and Perlmutter (1983), namely 0.041 s^{-1} (Sun et al., 2008a). Kyaw et al. (1998) calculated comparable reaction rates as well, with maximum conversion time derivatives below approximately 0.06 s^{-1} in a range of carbonation temperatures between 600°C and 800°C and in a range of CO_2 partial

pressures between 60 kPa and at 101 kPa. Additionally, these literature data suggest that the significant differences respect to the reaction rates presented in this work cannot be due to the different operating conditions used during the absorption process, mainly the partial pressure of CO₂ and the carbonation temperature. In fact, Kyaw et al. (1998) explored operational conditions similar to the values used in this study (partial pressure of CO₂ equal to 101 kPa). Further, Sun et al. (2008a) analyzing their experimental data noted that the CaO carbonation intrinsic kinetics can be described as a zero-order reaction respect to the CO₂ partial pressure (relative to the equilibrium partial pressure), when such quantity is equal or higher than 10 kPa, confirming that the high reaction rates (conversion time derivatives between 0.280 s⁻¹ and 0.239 s⁻¹) measured in this work cannot be ascribed to the pure CO₂ atmosphere used to carry out the carbonation experiments.

The explanation of such high carbonation rates is more reasonably found considering the characteristic geometry of the flow cell/furnace used to perform the carbonation experiments in this work. Thus far, the most popular and widely used approach to investigate the CaO-CO₂ reaction has been the thermo-gravimetric analysis (TGA). To the best of our knowledge, all the kinetic studies on the carbonation reaction available in literature are based on thermo-gravimetric experiments (Bathia and Perlmutter, 1983, Kyaw et al., 1996, Kyaw et al., 1998, Sun et al., 2008a, 2008b, Grasa et al., 2009, Wu and Lan, 2012). With this technique, carbonation experiments are typically carried out feeding in a reaction chamber/furnace a reacting mixture of CO₂ in nitrogen or pure CO₂, and the CaO sorbent reactivity is measured by recording the change in sample weight due to the carbon dioxide absorption such that the monitored weight increase, as a function of a controlled gas atmosphere and of a temperature/time program, is related to the progress of the carbonation. Preliminary tests are usually performed to identify the operating conditions required to reduce/eliminate the physical limitations (external, inter-particle, intra-particle mass diffusion) that can affect TGA measurements. In particular, the external mass transfer, which limits the gas (CO₂) diffusion towards the solid sorbent (CaO) surface, cannot easily experimentally eliminated and still calls into question the quality of the CaO conversion versus time profiles thus far obtained with this

technique. The external mass transfer is related to the total gas flow rate and it is typically reduced applying high gas flow rates. However, even when working at high gas flow rates, thus far it has not been demonstrated that the local velocities inside the TGA sample holder (i.e. above the sorbent particles) are high enough to support a high CO₂ consumption rate due to the rapid surface chemical reaction (namely, CaO carbonation). Even though a few authors (Sun et al., 2008a, Grasa et al., 2009) claim that their TGA experimental data (conversion versus time curves) are independent of the gas flow rate (using high flow rates), in our opinion such results could be still dependent on the external mass diffusion.

On the contrary, in this study the carbon dioxide was forced to flow inside a capillary, directly through the sample particles with high gas velocities around the sample particles, so that it can be reasonably assumed that the external CO₂ mass transfer limitation was minimized (likely it was completely eliminated). Specifically, the flow rate used in each experiment provided a gas (CO₂) velocity of around 20 cm/s (in normal conditions) at the capillary inlet. Therefore, it can be assumed that the experimental data presented in this work represent the surface chemical reaction step, namely the intrinsic carbonation reaction rate.

3.4 Effect of the initial CaO average crystallite size on the reaction rate

The maximum conversion rates presented in the previous section 3.3 are plotted in Figure 11 as a function of the average crystallite size of the corresponding CaO samples at the beginning of each carbonation run.

As shown in Figure 11, even though the data look somehow scattered, it seems reasonable to identify a relationship of inverse proportionality between the maximum conversion rates and the average size of the CaO crystalline domains.

An hypothesis to explain such relationship is that the initial carbonation conversion rate (which can be estimated by the maximum conversion rate) is related to the active (not the total) specific surface area that characterizes the sorbent particle internal surface and that the active surface area depends

on the initial CaO crystallite size. Specifically, according to such hypothesis, smaller CaO crystallite sizes indicate a larger length of crystallite boundaries per unit of surface area and consequently a larger active specific surface area for the occurring CaO-CO₂ reaction, the number of reactive sites being proportional to the length of crystallite boundaries. This would result in an increase of the reaction rate per unit of surface area. In support of such hypothesis, Mess et al. (1999), in an investigation on the product layer diffusion during the carbonation reaction of non-porous calcium oxide, modeled the reaction between CO₂ and CaO assuming that a contribution to the conversion rate is proportional to the access of the carbon dioxide to the calcium oxide surface by grain boundary diffusion, which was in turn proportional to the grain boundary length per unit of surface area. Also in their work the grain boundary length per unit of surface area was assumed to be inversely proportional to the grain size.

4. Conclusions

In this work, the time-resolved synchrotron radiation x-ray powder diffraction (SR XRPD) technique was applied for the first time to the CO₂ carbonation reaction, alternatively to the thermogravimetric analysis (commonly used in literature for such studies), to investigate the kinetics of the chemical transformations during the CO₂ absorption process and to simultaneously measure the calcium oxide crystallite size. Specifically, the CaO conversion profiles were estimated applying the Rietveld refinement method on the synchrotron x-ray diffraction data collected at the beamline 17-BM-B of the Advanced Photon Source (APS) at the Argonne National Laboratory.

The study of the carbonation curves (obtained in the temperature range between 450°C and 750°C, at a CO₂ partial pressure of 1 bar) has pointed out that the reaction rates of the characteristic rapid first stage of the carbonation are surprisingly higher than the typical values reported in the literature, obtained by TGA. An average maximum conversion time derivative of about 0.280 s⁻¹ ($\pm$ 13.2% of standard deviation) was observed, which is about five times higher than the values thus far reported in literature (Bathia and Perlmutter, 1983, Kyaw et al., 1996, 1998, Sun et al., 2008a).

This result highlights that the capillary system/flow cell furnace used to carry out the CO₂ absorption experiments allowed to minimize (up to probably eliminate) the external mass transfer limitations that instead likely affected the CaO carbonation results thus far obtained by TGA. The external mass transfer limitations were minimized thanks to the high gas velocity around the CaO sorbent particles that reasonably supported the high CO₂ consumption rate due to the surface chemical reaction. Therefore, it can be stated that the experimental data (conversion-time curves) presented in this work represent the intrinsic chemical kinetics of the carbonation reaction (due to surface chemical reaction).

In addition, the dependence of the conversion-time curves on the initial (at the beginning of carbonation) crystallite size was investigated. Specifically, the final conversion of the calcium oxide particles was compared with the average size of the CaO crystalline domains measured at the beginning of the carbonation reaction. The comparison shows that the lower is the initial average crystallite size of the fresh calcium oxide, the higher is the conversion of the sorbent particles evaluated at the end of the absorption experiments. The obtained linear relationship between the final conversion and the initial CaO crystallite size was found to be independent from both the carbonation temperature maintained during the experiments and from the operating conditions used to produce the initial CaO sorbent particles from commercial calcium carbonate. Consequently, the initial CaO crystallite size is likely a good indicator of the initial particle porosity, which determines the final maximum conversion reachable. Finally, an hypothesis was formulated to explain the dependence of inverse proportionality between the initial/maximum conversion rates and the initial CaO crystallite size. According to such hypothesis, small CaO crystallites imply a high crystallite boundary length per unit of (internal) surface area, which would determine a high number of active sites for the carbonation, namely a high active specific surface area, and consequently a high conversion rate. This hypothesis needs to be further elucidated and validated, particularly through the analysis of the calcium carbonate crystallite size trends during the carbonation.

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Figure Captions

Figure 1: Typical profile refinement for a diffraction pattern obtained at a CaO conversion of 20% and at a carbonation temperature of 450°C. Measured (black crosses) and calculated (red solid line) values are compared (their difference is plotted by the blue solid line). The position of the Bragg peaks for CaCO₃ and CaO are shown by pink and cyan blue dots respectively.

Figure 2: Calcium oxide conversion for isothermal carbonation at different temperatures (calcination at 900°C for 5 min). Profiles corresponding to 20 min (left) and 10 s (right) of carbonation.

Figure 3: Calcium oxide conversion for isothermal carbonation at different temperatures (calcination at 900°C for 60 min). Profiles corresponding to 20 min (left) and 10 s (right) of carbonation.

Figure 4: Calcium oxide conversion for isothermal carbonation at different temperatures (calcination at 700°C for 60 min). Profiles corresponding to 20 min (left) and 10 s (right) of carbonation.

Figure 5: Calcium oxide conversion for carbonation at 650°C using sorbents with different initial CaO crystallite size. Profiles corresponding to 20 min (left) and 10 s (right) of carbonation.

Figure 6: Calcium oxide conversion for carbonation at 550°C using sorbents with different initial CaO crystallite size. Profiles corresponding to 20 min (left) and 10 s (right) of carbonation.

Figure 7: Calcium oxide conversion for carbonation at 450°C using sorbents with different initial CaO crystallite size. Profiles corresponding to 20 min (left) and 10 s (right) of carbonation.

Figure 8: Relationship between the final CaO conversion and the initial CaO average crystallite size. The solid line represents a linear fitting of the results for runs in which conversion was not significantly increasing at the end of carbonation (black circles). Red crosses represent runs in which conversion was still increasing at the end of carbonation.

Figure 9: Theoretical estimation of the initial CaO porosity from the initial CaO average crystallite size. The solid line represents a linear fitting of the results for runs in which conversion was not significantly increasing at the end of carbonation (black circles). Red crosses represent runs in which conversion was still increasing at the end of carbonation.

Figure 10: Linear fitting of the first part of the CaO conversion profiles, used to estimate the initial conversion rates in the first stage of carbonation. Example on the conversion curve at a carbonation temperature of 450°C.

Figure 11: Maximum conversion time derivatives as a function of the CaO average crystallite size at the beginning of carbonation.

Table Captions

Table 1: Summary of experimental operating conditions and corresponding results (final conversion and CaO average crystallite size at the beginning of carbonation) obtained by Rietveld refinement.

Table 2: Initial conversion time derivatives estimated from experimental profiles of CaO conversion (X) as a function of the reaction time (t) during the first rapid carbonation stage.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Table 1

Run	Calcination		Carbonation	Final CaO conversion	Initial CaO Average Crystallite Size
	T [°C]	t [min]	T [°C]	X [-]	[nm]
A	900	5	450	0.63	39 (± 2)
B	900	5	550	0.26	100 (± 3)
C	700	60	650	0.72	29 (± 2)
D	700	60	450	0.63	38 (± 2)
E	700	60	550	0.58	61 (± 3)
F	900	5	500	0.21	109 (± 2)
G	900	5	750	0.57	156 (± 3)
H	900	60	650	0.42	255 (± 5)
I	900	60	450	0.07	124 (± 2)
J	900	5	650	0.64	52 (± 2)
K	750	5	650	0.75	31 (± 2)
L	800	5	650	0.71	35 (± 2)
M	900	60	550	0.53	44 (± 1)
N	900	5	600	0.66	50 (± 2)
O	700	60	500	0.19	63 (± 3)

Table 2

Run	dX/dt [s ⁻¹]		
	Maximum	Linear fitting up to 25% of the final CaO conversion	Linear fitting up to 50% of the final CaO conversion
A	0.391	0.261	0.317
B	0.242	0.185	-
C	0.221	0.198	0.150
D	0.541	0.336	0.427
E	0.468	0.420	0.387
F	0.239	0.239	-
G	0.106	0.067	0.060
H	0.216	0.192	0.196
I	0.040	0.028	-
J	0.180	0.118	0.140
K	0.207	0.170	0.160
L	0.320	0.221	0.223
M	0.377	0.298	0.311
N	0.333	0.282	0.283
O	0.314	0.362	-
Average	0.280 (± 13.2% stand. dev.)	0.239 (± 9.6% stand. dev.)	0.240 (± 11.4% stand. dev.)