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The decrease of carbonation efficiency of CaO along calcination–carbonation cycles: Experiments and modelling

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ABSTRACT

Successive calcination–carbonation cycles, using CaO as sorbent, have been performed either in a classical fixed bed reactor or using a thermogravimetric analyser. Significant differences in carbonation efficiencies were obtained, possibly due to different conditions prevailing for CaO sintering during the calcination stage. The effect of the presence of CO_2 on sintering was confirmed.

A simple model of the decay of the carbonation capacity along cycles based on the specific surface area of non-sintered micrograins of CaO is able to predict the decrease of the extent of conversion obtained after 40 carbonations along calcination–carbonation cycles. The asymptotic extent of conversion is obtained when all the micrograins present within a grain are sintered. A detailed model of the carbonation shows that the voids present between the micrograins are filled up by carbonate when a critical thickness of the carbonate layer around each micrograin reaches 43 nm. Then, carbonation becomes controlled by diffusion at the scale of the whole grain, with the CO_2 diffusion coefficient decreasing (at 650 °C) from 2×10^{-12} to $6.5 \times 10^{-14}\,m^2/s$ as carbonation proceeds from 50% conversion to 76% (first cycle). This scale change for diffusion is responsible for the drastic decrease of the carbonation rate after the voids between micrograins are filled up.

1. Introduction

For environmental reasons, there is now a deep interest in the capture of CO_2 emitted by large stationary industrial combustion sources (Herzog, 2001). One strategy is to use sorption–desorption cycles with a suitable sorbent, such as CaO (Stanmore and Gilot, 2005). During these cycles, CO_2 is separated from the combustion gases as $CaCO_3$ obtained by carbonation of CaO in the temperature range of 600–700 °C. The sorbent CaO is regenerated by calcination of limestone in another reactor operated at a higher temperature (850–950 °C). Energy for calcination can be supplied by oxycombustion to produce a highly concentrated CO_2 stream suitable for being compressed and stored. Other sorbents, such as dolomite or dolostones, have been tested (Fennel et al., 2007). Criteria for the choice of the sorbent are its cost and its ability to maintain high capture efficiency along cycles to minimize the fresh sorbent consumption by the system (Abanades et al., 2004).

The reversible reaction $CaCO_3 \leftrightarrow CaO + CO_2$ has been extensively studied. Carbonation of CaO is a two step reaction with a fast stage followed by a slow one which does not go to completion (Barker, 1973). The second stage is controlled by diffusion of CO_2 within the product layer (Bhatia and Perlmutter, 1983; Barker, 1973; Fennel et al., 2007; Sun et al., 2007). Carbonation seems to occur in two different regions, the first is microporosity within grains and the second is grain boundaries and walls of large pores within the grains (Abanades and Alvarez, 2003). Carbonation in the microporosity stops when $CaCO_3$ has filled up the available microporosity. This limiting microporosity is used by Bhatia and Perlmutter (1983) to predict the carbonation conversion after a single calcination. Carbonation in the second region is limited by diffusion of CO_2 through the product layer. The critical thickness of the product layer covering the walls of pores has been determined by Alvarez and Abanades (2005a), using a cylindrical pore model. The data provided by Hg porosimetry for different carbonated (stopping carbonation at the end of the fast stage) and corresponding calcined samples were used to estimate the carbonate thickness deposited on the walls of CaO pores. A value equal to 49 nm was proposed whatever the limestone type. Barker (1973) also proposed a value equal to 22 nm, accounting in a very simple way only on the expansion of the solid due to the different molar volumes of CaO and $CaCO_3$, and on the total surface available for reaction. This value is questionable since some pores may be filled or blocked (bottlenecks) before this critical thickness has been reached (Alvarez and Abanades, 2005b). The carbonation efficiency is related to the pore size distribution

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(Bhatia and Perlmutter, 1983). Small pores, narrower than 150 nm, between micrograins, are supposed to play an important role in the carbonation process (Fennel et al., 2007). Calcination of limestone always proceeds to completion. Its rate is affected by temperature, CO_2 partial pressure, total pressure and particle diameter (García-labiano et al., 2002; Darroudi and Searcy, 1981).

The maximum extent of carbonation decreases with the number of calcination/carbonation cycles (Abanades, 2002; Abanades and Alvarez, 2003; Alvarez and Abanades, 2005a,b), due to a loss of porosity associated with small pores, linked to an increase of the fraction of larger pores formed within the calcined grains (Abanades and Alvarez, 2003). A model of this microporosity loss by sintering (or grain shrinking) leads to the following equation ($X_N = f_m^N(1-f_w)+f_w$) (Abanades and Alvarez, 2003). The maximum carbonation conversion X_N obtained after cycle number N depends only on two parameters f_w and f_m which are fitted to experimental results: $f_w = 0.17$ and $f_m = 0.77$. The second parameter f_m is associated with the ratio of microporosity to the total porosity produced during calcination. Sintering of CaO during calcination is responsible for the microporosity loss (Agnew et al., 2000; Lysikov et al., 2007). The presence of carbon dioxide and water vapour increases the rate of sintering (Mai and Edgar, 1989). Their combined effects are additive (Borgwardt, 1989). Mai and Edgar (1989) have proposed a model to calculate the surface area evolution during calcination of calcium hydroxide. Sintering of CaO and CaO formation by calcination was coupled, and the sintering kinetic constant was obtained by fitting calculated surfaces areas to measured ones. Agnew et al. (2000) applied the same model to $CaCO_3$ calcination and sintering. A wet precipitation process was investigated to synthesize a high-surface area calcium carbonate, which produced a sorbent able to maintain a high carbonation conversion during cycling (Gupta and Fan, 2002). Heat and mass balances in the system for CO_2 capture were performed to define the best option to optimize the process (Rodriguez et al., 2008). A compromise must be found between the increase of the carbonation efficiency by continuous fresh limestone addition and the additional heatdemand for calcination of this material.

A comparable cycling process was proposed by Nikulshina et al. (2009). To capture CO_2 from atmospheric air in a fluidized-bed reactor.

In contrast to the work of Nikulshina et al. the aim of this work is the capture of CO_2 emitted from stationary sources. In consequence, a higher CO_2 concentration (20%) was chosen.

The objective of this work is to establish a simple model, accounting for CaO sintering, and able to predict the carbonation efficiency along calcination–carbonation cycles. The experimental results will be discussed on the basis of a new rate model for carbonation.

2. Experimental

A Mexican limestone (Tamuin) has been used. The percentage of CaO in this material is 53.50 wt% and the CO_2 content (determined by thermogravimetric analysis, TGA) is 42.48 wt%. The MgO mass fraction is 0.46 wt%. Impurities, such as silica (0.65 wt%), alumina (0.18 wt%), Fe_2O_3 (0.12 wt%), sulphur (0.10 wt% in SO_3 equivalent), and others (< 0.10 wt%) are also present.

The raw material was crushed and sieved. The particle size interval 125–160 μm in diameter was selected for experiments. This diameter range was chosen to avoid CO_2 transport limitations within the particles.

Successive calcination–carbonation cycles were performed in a classical fixed bed reactor. For each run, 5 g of limestone were loaded on a frit located in the isothermal section of a cylindrical reactor (16 mm ID) surrounded by an oven. The thickness of the sample bed was 18 mm. The temperature was recorded by a K type thermocouple located in the centre of the sample bed. For the first calcination, temperature was increased from ambient to the chosen temperature (850 °C) at roughly 20 K/min under a nitrogen flow equal to 100 N l/h. All flow rates were controlled by BROOKS mass flow controllers. Then, temperature was maintained for 40 min at 850 °C. During this stage, CO_2 emissions were analysed with an Infrared Rosemount NGA 2000 Analyser. At the end of this temperature stage, no more CO_2 emissions were detected, proving that calcination was complete. After cooling to carbonation temperature (650 °C), the gas flow was switched to a mixture (100 N l/h) containing 20% CO_2 in nitrogen. The calcined sample was then exposed to the reacting gas mixture during 30 min for carbonation.

The final extent of carbonation at the end of this first cycle was determined with a SETARAM thermogravimetric analyser, which gives better precision than the determination by integration of CO_2 emissions during carbonation. Roughly 20 mg of the carbonated material were taken out from the reactor after cooling and were injected in the crucible of the thermogravimetric analyser. The cylindrical quartz crucible was 6-mm diameter and 1.5-mm high. Temperature was recorded by a type K thermocouple located 1 cm under the crucible. Temperature was increased from ambient to 850 °C at 20 K/min under a nitrogen stream (5 N l/h) to complete calcination. From the measured weight loss, the extent of carbonation, in percent of CaO moles converted to $CaCO_3$, was calculated. To obtain the specific surface area measurements a new 5-g sample was introduced into the reactor. After calcination the sample was cooled to room temperature. The sample was then submitted to BET surface area measurements.

To obtain the efficiency of carbonation number i after i calcinations, a new 5-g sample was introduced into the reactor and the sequence calcination–carbonation was repeated i times. Then 20 mg were taken out to be calcined in the thermobalance to measure the carbonation efficiency after i cycles.

To obtain the specific surface area measurements after i calcinations a new 5-g sample was introduced in the reactor. The sequence calcination–carbonation was repeated $(i-1)$ times. After a final calcination the sample was cooled to room temperature, and then submitted to BET surface area measurements.

The extent of carbonation was determined for i equal to 1, 5, 10, 25 and 40.

The same procedure was repeated for two other calcination temperatures, 750 °C maintained during 95 min (to ensure a complete calcination) and 950 °C maintained during 35 min. For the experiments involving the temperature 750 °C, no more than 10 cycles were performed with determinations of the extent of carbonation carried out after calcinations 1, 2, 3, 4, 5, and 10. For calcinations at 950 °C, no more than three cycles were performed with determinations of the extent of carbonation carried out after cycles 1, 2, and 3.

Additional experiments consisting of the first cycle only (one calcination and one carbonation) were also conducted. In these experiments, the duration of the calcination stage was modified from 20 min to 8 h for different calcination temperatures to investigate the effect of sintering on the final extent of carbonation of the sample.

The morphology and size of the particles were determined by scanning electron microscopy using a Philips XL30 microscope with a field emission gun.

The BET surface area of the obtained calcined samples along the different cycles was measured using a Micromeritics ASAP 2010 analyser, at −196 °C, with nitrogen as adsorbent. BJH analysis was performed to investigate the pore size distribution for pores in the range of 2–150 nm.

Another series of 30 cycles was performed with the SETARAM thermogravimetric analyser. A small (4–6 mg) sample was submitted to pure nitrogen (calcination) or 20% CO_2 in nitrogen (carbonation) at a flow rate equal to 5 N l/h. For the first calcination