

MULTICYCLIC STUDY ON THE CARBONATION OF CaO USING DIFFERENT LIMESTONES

K. Chrissafis*

School of Physics, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

Different samples of limestones, with small differences in their stoichiometry, have been studied comparatively. The carbonation reaction has been studied for a large area of isothermal temperatures. The conditions for the multicyclic experiments of calcination/carbonation were: isothermal temperature 670°C, heating time 60 min and carrier gas CO₂. The final carbonation conversion depends mainly on the isothermal temperature of the carbonation reaction and the heating time. The final temperature of the calcination reaction depends on the percentage of CaO that it has not been converted to CaCO₃ in the repeated carbonation experiments. The quantity of CaO that has not been carbonated, in the same sample, affects the values of the coefficients of the kinetic model that fit the calcination reaction. In the multicyclic experiments the carbonation conversion for two of the four studied samples, was high enough in comparison to other samples of calcite. At sample A the reduction of the carbonation conversion during the first five cycles is less than it is at other samples from the literature. Under the above experimental conditions – isothermal temperature and heating time – specific samples consisted mainly of calcite can absorb larger quantities of CO₂ than samples consisted mainly of dolomite.

Keywords: calcination, carbonation, limestones, multi-cycles, TG

Introduction

During last years there is an increasing interest for the greenhouse effect. For this reason the industry gives an important role to the capture of CO₂ through the carbonation reaction of CaO. The CO₂ separation from flue gas [1] or from syngas [2], the storage of energy [3, 4], chemical heat pump [5–8], and the clean hydrogen production by reaction integrated coal gasification [9, 10] are some of the applications for which the above carbonation reaction has been studied.

The extent of carbonation reported in many studies shows considerable variation [11–28]. A variety of isothermal and non-isothermal measurements were used in these studies, which examine the reversibility of the decomposition of calcium carbonate after a number of cycles of calcination/carbonation. The carrier gas used for carbonation was CO₂, or a combination of CO₂, N₂ and air in various proportions, and for calcination, CO₂ or N₂. The factors that were examined for their effect on the extent of carbonation refer to the temperature at which the isothermal measurements were done, the pressure of the carrier gas, the proportion of the gases of the carrier gas, the pore volume, the surface area, the sintering effect etc. Several studies on the reversibility of the carbonation/calcinations reaction showed that the recarbonation is not fully reversible [1, 8, 18–28]. The conversion decreases rapidly with the number of carbonation/calcination cycles.

There are not any references in the literature for the influence of the slight differences in stoichiometry in limestones and commercial calcite on the final carbonation conversion and its reduction in the multicyclic experiments.

The aim of this article is the study of the reversibility of the calcination/carbonation reaction after multicyclic experiments. Three natural limestones and one commercial calcite with slight differences in their stoichiometry have been used. The total value of the absorbed CO₂ in these samples has been compared with respective results in dolomite samples from the literature.

Experimental

Three of the studied samples were collected from the Kozani broader area (north-western Macedonia, Greece). Sample A was collected from carbonate formations of the Vermion Mountain; B belongs to the quarried limestone formations of Vourinos Mountain, while C belongs to carbonate formations nearby the mountain of Vourinos. Samples A, B and C can be characterized generally as limestones [29, 30]. The fourth sample was commercial calcite (CaCO₃) produced by Aldrich and from now on it will be referred to as sample D. The samples have been selected in such a way so as to have slight differences

* hrisafis@physics.auth.gr

in their stoichiometry. Also, the samples have small quantities of Mg in order the influence of the small percentage of dolomite to be determined.

Thermogravimetric analysis was made with a Setaram SETSYS TG-DTA 1750°C. The samples, in powder form with grain size smaller than 40 μm (measured by sieving), were placed in alumina crucibles. An empty alumina crucible was used as reference. The mass of each sample was about 15 mg and the heating and cooling rates were 10°C min⁻¹. The conditions for the experiments were:

- Isothermal carbonation: Samples were heated from ambient temperature to 920°C using N₂ as carrier gas, then they were cooled to the desired isothermal temperature at the same rate used for heating and under the same gas. The CO₂ was used as carrier gas in the isothermal experiments.

Multi-cycles experiments: The first cycle is the same as in the isothermal carbonation. For the next cycles, the only difference was that the samples were heated from the isothermal temperature, 670 to 920°C and not from ambient temperature.

Chemical analysis of the rock samples was performed by Atomic Absorption Spectroscopy (AAS) using a Perkin-Elmer 5000 apparatus.

Results and discussion

The results of the chemical analysis of the three limestones showed that the main contribution in all studied samples is from Ca and the amount of impurities that ranges between 1.0 and 1.5% is attributed to the low grade of metamorphism (greenschist face) of the rocks.

The stoichiometries of the studied samples they have been inferred by measurements of mass loss are presented in Table 1. By measuring the mass loss, dolomite has been verified with satisfactory accuracy only in sample B. The experiments for the verification of dolomite have been made using CO₂ as carrier gas, because under this condition the calcination of dolomite are completed in two separate steps [30]. Sample B was especially selected, with a minimum quantity of dolomite that can be measured, in order to verify whether dolomite or MgO has an influence on the carbonation reaction of the samples.

Table 1 Participation of the constituents in three limestones and commercial calcite using TG

Sample	Calcite/%	Dolomite/%	Other/%
A	98.4	0.0	1.6
B	97.9	1.6	0.5
C	99.2	0.0	0.8
D	99.2	0.0	0.8

During calcination and carbonation reactions possible differences for the four samples have been explored. In Fig. 1 the calcination reaction for all the studied samples is presented. The main difference at these plots is that the end temperature of the calcination for sample A is about 20°C higher than it is for the other samples. Figure 2 profiles the carbonation conversion of CaO with increasing isothermal reaction temperature for sample A which isn't fully reversible. According to the literature, this behavior can be qualitatively explained on the basis of the changing structural properties of the solid reactant. In principle, pore volume created during calcinations should be sufficient to permit complete recarbonation of the CaO. In practice, however recarbonation occurs preferentially near the particle exterior so that, as the surface porosity approaches zero, CO₂ is prevented from reaching unreacted CaO at the interior of the particle. Sintering of either or both the CaO and CaCO₃ may also contribute to pore closure [23]. The final percentage of carbonation conversion, according to the above model of reaction, depends on the maximum calcination temperature, the isothermal carbonation temperature and the heating time. Above a value of isothermal temperature (640°C), almost the total quantity of CaO has already been converted into

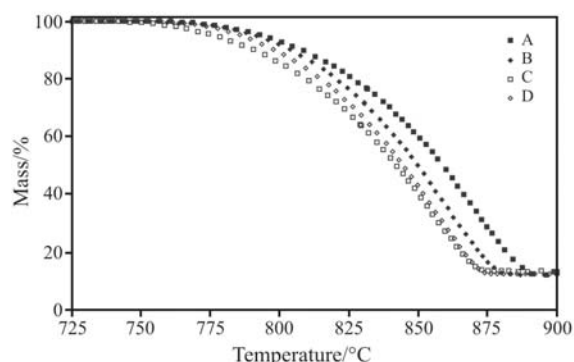


Fig. 1 TG curves of the four studied samples during calcinations

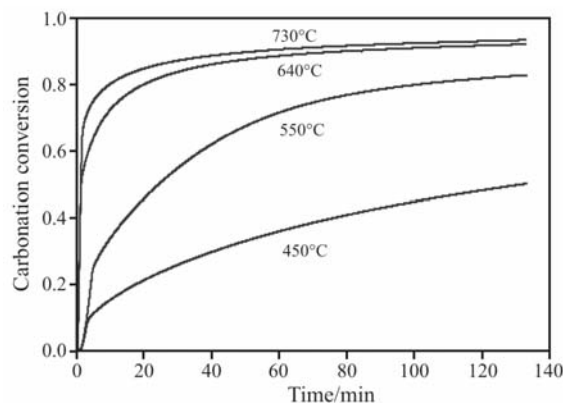


Fig. 2 Carbonation conversion for sample A in four isothermal temperatures

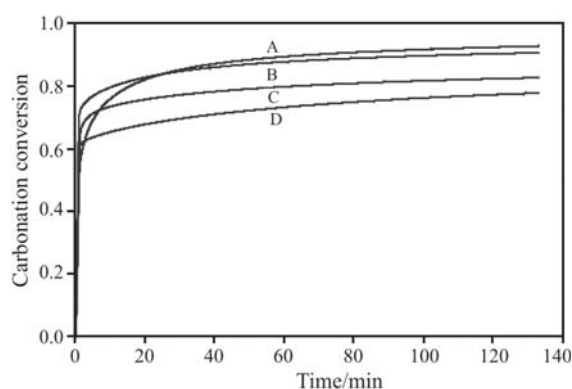


Fig. 3 Carbonation conversion for the four studied samples in isothermal temperature of 670°C

CaCO₃ in 60 min time. For the multicyclic experiments, smaller isothermal temperatures and heating time can be chosen using the above conclusions.

In Fig. 3, the carbonation reaction for the four studied samples can be seen comparatively, at the isothermal temperature of 670°C. Almost the maximum carbonation was achieved for all the samples within a few minutes of reaction. Only in the shape of sample A there is a slight difference. After the first rapid increase of carbonation a slower increase followed, in comparison with the other three samples. The maximum carbonation conversion according to the literature is between 70–80% for samples of calcite, while percentages above 90% are referred to only when the samples were heated for 24 h [20] or when the precipitated calcium carbonate was used [1]. Conversions above 90% have been referred in the literature for samples of dolomite [31]. The carbonation conversion values for samples C and D are in the same area with the ones at the literature measured under analogous conditions, but the conversion values in samples A and B are considerably higher. This is very interesting since these high conversions have been predicted in a very short time, 60 min, compared to 24 h and without any commercial treatment as for the precipitated calcite. The high carbonation conversion in sample B is analogous with values from samples consisted mainly of dolomite, although the quantity of dolomite is very small (1.6%) at this sample. Maybe, this can be connected to the existence of MgO, from the dolomite. According to [23, 31, 32] this behavior is attributed to the excess pore volume produced during the initial decomposition of MgCO₃ and to a reduction in the sintering rate due to MgO. Smaller quantities of Mg exist also in the other two limestones according to the chemical analysis results. According to Silaban and Harrison [23], substitution of dolomite for CaCO₃ as the sorbent precursor may prove effective both in increasing the fractional conversion of calcium and in reduction the rate of deterioration.

According to the literature a large variety of different conditions in the multicyclic experiments of carbonation, have been used [1, 8, 18–28] with a great dispersion in the recarbonation conversion. Comparative results have not been presented for samples with slight differences in their stoichiometry in the literature. According to the literature the carbonation conversion depends mainly on the isothermal temperature and the heating time. For this reason the isothermal temperature of 670°C has been chosen, which is one of the lower temperatures with high carbonation conversion. Also, the heating time was 60 min since, as it can be seen in Fig. 3, after this time the increase of carbonation conversion is negligible. This time is also necessary, because in sample A the carbonation conversion has its higher values later than sample B (Fig. 3) and for comparison reasons the chosen heating time must be the same and the carbonation conversion also of high values. The reduction of the heating time and the isothermal temperature reduces the possibility of the influence of sintering and also reduces the cost of the commercial use.

There is a special interest in the repeated cycles of calcination and carbonation. Samples A and B which have shown the higher percentage of carbonation have been studied for this part. The percentage of the CaO which absorbs CO₂ was studied in 25 cycles of calcination and carbonation. After all the cycles of calcination, the mass that remains is the same with that after the first calcination. That means that all the re-carbonated CaCO₃ has been calcinated again. In the re-calcination reactions seems to be a relation between the quantities of CaO that have not been carbonated and the final temperatures of the calcination of CaCO₃. As the quantity of CaCO₃ that exists in the sample is reduced or the quantity of CaO that has not been carbonated is increased, the final temperature of the calcination is reduced (Fig. 4). This difference, between the first and the twenty fifth cycle of calcination, is 15°C for sample A. The calcination conversion has been cal-

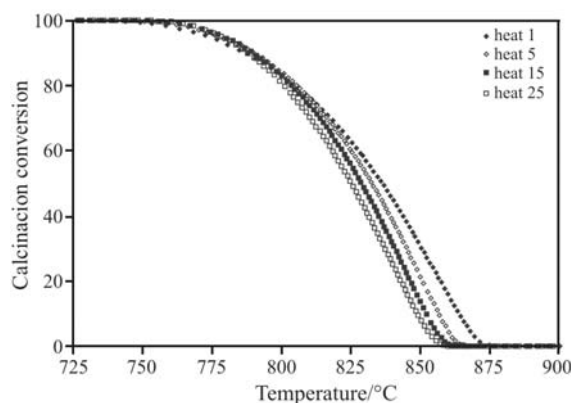


Fig. 4 Calcination conversion for sample A for four different calcinations cycles

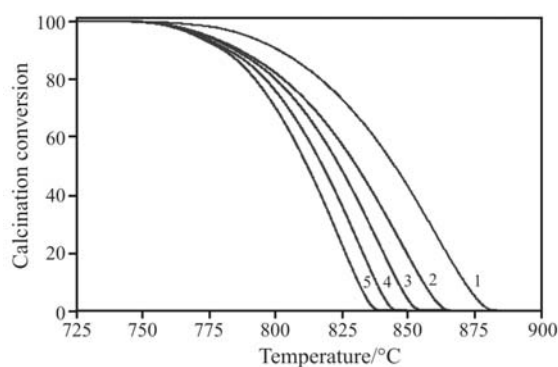


Fig. 5 Calcination conversion for sample B for five different calcination cycles. 1 – 1st cycle, 2 – 2nd cycle, 3 – 5th cycle, 4 – 15th cycle and 5 – 25th cycle

culated in relation to the total quantity of CaCO_3 that exists in the sample after every cycle of calcination/carbonation. The differences in the shape of the plots and the end temperatures affect the values of the kinetic coefficients (activation energy E , pre-exponential factor A) of the kinetic model that fits the calcination reaction. From these plots we can conclude that although we refer to samples consisted mainly of calcite and the calcination reaction has been done under the same conditions, the kinetic coefficients seem to be affected by the quantity of CaO that has not been carbonated which is connected with the pore volume and the sintering effect after every cycle.

The calcination reaction for sample B can be seen in Fig. 5. The difference between the first and the twenty fifth cycle in the final temperature of calcination reaction has been increased to 43°C . This difference must be expected, as in sample A, to produce enough differences to the kinetic coefficients.

In Fig. 6 the calculated values of the carbonation conversion at samples A and B are presented comparatively. For comparison reasons, the results of the re-carbonation of a typical dolomite sample [28], with code name E, have been included in the same plot. The stoichiometry of this sample was: dolomite 95.5%, calcite 3.9%. The two studied samples, A and B, show a large difference in the carbonation conversion although the quantity of calcite is almost the same. The dependence of the carbonation conversion on the number of cycles for the three samples (A, B, E) can be described by a second degree exponential function, but the constant coefficients are different for every sample. The carbonation conversion dependence in these samples can not be described with the function and the coefficients that they have been given by Abanades [21] in his article. For these samples the reduction of the carbonation conversion is greater and qualitatively the shape of these plots seems to be nearer to the dependence for sample B in this work. Especially, the difference is in the first 3–4 cycles of carbonation, since

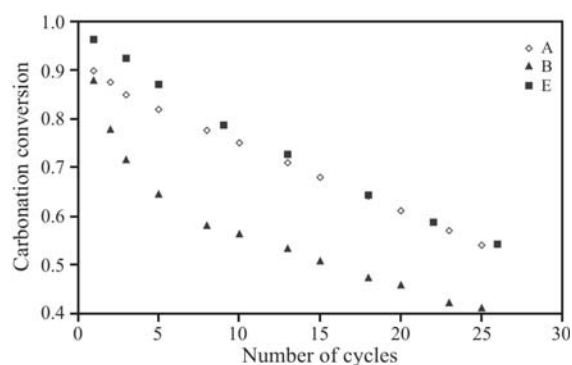


Fig. 6 Carbonation conversion for samples A, B, E in multi-cycle experiments

sample A mainly seems to be behaving like the sample with dolomite. The existence of Mg , mainly in sample B, does not seem to be finally the factor that increases the capability of carbonation conversion, since in this sample the reduction of the carbonation conversion in the first cycles is greater, in contrary to the samples consisted mainly of dolomite, sample E.

According to the literature the total capability of the dolomite samples to absorb CO_2 is higher than in the calcite [31]. According to the stoichiometry of the samples, in 100 g of starting material the quantity of CaO is 55.13, 55.34 and 31.23 g for the samples A, B and E, respectively. The total quantity of CO_2 that can be absorbed after 25 cycles from samples A and B is much greater than that from sample E, if the above quantities of CaO are used. As this is connected with the starting quantity of CaO , it is not obvious from the plots in Fig. 6 especially for sample B. So the conclusion is that, under specific conditions – isothermal temperature, heating time – specific limestones can absorb larger quantities of CO_2 in comparison with samples of dolomite. It is obvious that the use of carbonated rocks as starting materials does not help the study of the influence of the different constituents, which exist in the samples, to the carbonation conversion.

Conclusions

The four samples that have been studied comparatively showed differences in the calcination and carbonation reactions. The final percentage of carbonation depends on the isothermal temperature and the heating time. The final temperature of the calcination reaction depends on the percentage of CaO that it has not been converted into CaCO_3 in the repeated carbonation experiments. The quantity of CaO that has not been carbonated, in the same sample, affects the values of the coefficients of the kinetic model that fits the calcination reaction. In the multicyclic experiments the carbonation conversion for two of the four studied sam-

ples was high enough in comparison with other samples of calcite. Under specific conditions, isothermal temperature and heating time, samples consisted mainly of calcite absorb larger quantities of CO₂ than samples consisted mainly of dolomite. This is very interesting since these high percentages have been produced in a very short time, 60 min, compared to 24 h and without any commercial treatment as for the precipitated calcite.

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Received: May 2, 2006

Accepted: June 1, 2006

OnlineFirst: October 20, 2006

DOI: 10.1007/s10973-006-7678-z