

The effects of procedural variables on the maximum capture efficiency of CO₂ using a carbonation/calcination cycle of carbonate rocks

K. Chrissafis^{a,*}, C. Dagounaki^b, K.M. Paraskevopoulos^a

^a Department of Physics, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

^b Department of Geology, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

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Abstract

The effect of procedural variables—mass and heating and cooling rate—on the maximum capture efficiency of CO₂ is studied, using a carbonation/calcination cycle, for a series of carbonation rocks with different stoichiometries of dolomite and calcite. The extent of carbonation and the cyclability depends particularly on dolomite presence and at the same time seems to be influenced by the existence of impurities. Samples having the highest percentage of calcite and the lowest percentage of impurities seemed to be independent on the above variables. In limestone samples with small quantity of dolomite, impurities or a combination of both of them was observed a very small increase in the extent of carbonation due to the increase in the initial mass of the samples, while these samples in the case of the same initial mass presented an increase in the extent of carbonation due to the decrease in the cooling and the second heating rate.

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1. Introduction

Fossil fuel is still the most important energy source. On the other hand it is also the major source for greenhouse gases that are assumed to cause global warming. So far, reliable methods for reducing the carbon dioxide emissions are a decrease in fuel consumption, increase in process efficiency or a change to renewable, CO₂-neutral fuel.

It is generally accepted [1] that the cost of the separation of CO₂ from flue gases introduces the largest economic penalty. This justifies a range of emerging approaches to separate CO₂ with more cost-effective processes. The CO₂ acceptor gasification process reached a demonstration phase [2] using the carbonation/calcination of CaO from limestones or dolomites to separate CO₂ from coal gasification gases. In these early processes, the release of CO₂ during calcination

was not an issue and the heat for calcination was supplied by partial combustion of the fuel with air. The need to obtain a purified stream of CO₂ from the calciner is relatively new. Shimizu et al. [3] proposed a cycle for combustion applications involving the regeneration of the sorbent in a calciner using CO₂/O₂ mixtures to burn part of the fuel. Silaban et al. [4] studied the reversibility of this reaction in dolomites and limestones as a base of a high temperature separation of CO₂ to produce hydrogen [4,5]. A similar process is being developed in Japan [6] that includes a carbonation/calcination cycle to produce H₂ from gasification. Finally, the reversible carbonation/calcination reactions have also been proposed as the base of energy storage systems [7] and as a chemical heat pump [8].

At higher partial pressures of CO₂ the thermal decomposition splits into a two stage process [9,10] as follows:



* Corresponding author. Tel.: +30 2310 998188; fax: +30 2310 994301.

E-mail address: hcrissafis@physics.auth.gr (K. Chrissafis).

The reversibility of the decomposition of calcium carbonate after a number of calcinations/carbonation cycles was examined in different studies [11–19]. The carrier gas used for the carbonation reaction was CO₂ or a combination of CO₂, N₂ and air in various proportions, and for calcination, CO₂ or N₂. In these studies was used a variety of non-isothermal and isothermal measurements and regarding the extent of carbonation, the reported results presented a remarkable variation. The factors that were examined for their effect on the extent of carbonation were the temperature at which the isothermal measurements were performed, the pressure of the carrier gas and the proportion of the gasses of the carrier gas [20,21]. The extent of the carbonation reaction was mainly connected with pore volume and surface volume of the sorbents, and was not examined in samples with different stoichiometries.

The aim of this article is to determine by non-isothermal measurements and by using CO₂ as the carrier gas, the extent of carbonation in naturally occurring carbonated rocks with different dolomite and calcite stoichiometries. Simultaneously, was studied the effect of two procedural variables, the sample mass and the heating–cooling rate, on the extent of carbonation. We examined the effect of these experimental variables during the carbonation, as others—carrier gas, pressure, isothermal temperature—that influence the process of calcination/carbonation, have already, been studied.

2. Experimental

Thermogravimetric analysis was made with a SETARAM SETSYS TG-DTA 1750 C. The samples in powder form with grain size smaller than 125 μm (measured by sieving), were placed in alumina crucibles. An empty alumina crucible was used as reference. Samples were heated from ambient temperature to 1100 C in a 50 ml/min flow of CO₂. Afterwards, they were cooled to the ambient temperature at the same rate used for heating and under the same gas. The heating–cooling cycle was immediately repeated for at least two more times, using exactly the same experimental conditions.

The studied samples—typical characteristic samples in each case—were collected from the Kozani broader area (northwestern Macedonia, Greece). In geotectonic terms, the area belongs to Pelagonian zone. Samples B-SE3, B-ME1, B-ME3 and B-ER5 were collected from carbonate formations of the Vermion Mountain. Samples K-RY1, K-AM1 and K-AM2 were collected from carbonate formations near the town of Kozani. Samples BO-BI2, BO-SX1 and BO-PA2 belong to the quarried limestone formations of Vourinos mountain, while samples BO-SE3, BO-PR3 belong to carbonate formations nearby the mountain of Vourinos. The samples B-SE3, B-ER5, BO-BI2, BO-SX1, BO-SE3, BO-PR3 are limestones while the B-ME1, B-ME3, K-RY1, K-AM1 and K-AM2 are dolomitic rocks. The sample BO-PA2 is characterized as dolomitic limestone [22].

Table 1
Percentage dolomite and calcite participation in different samples

	Dolomite (%)	Calcite (%)	Other (%)
B-ME3	95.5	3.9	0.6
B-ME1	89.6	9.7	0.7
K-RY1	89.5	10.2	0.3
K-AM1	86.6	13.2	0.2
K-AM2	85.8	14.0	0.2
BO-PA2	19.4	80.2	0.4
B-SE3	7.7	90.8	1.5
BO-SX1	2.0	97.8	0.2
BO-BI2	1.6	97.9	0.5
BO-PR3	1.0	98.4	0.6
B-ER5	0.0	98.4	1.6
BO-SE3	0.0	99.8	0.2

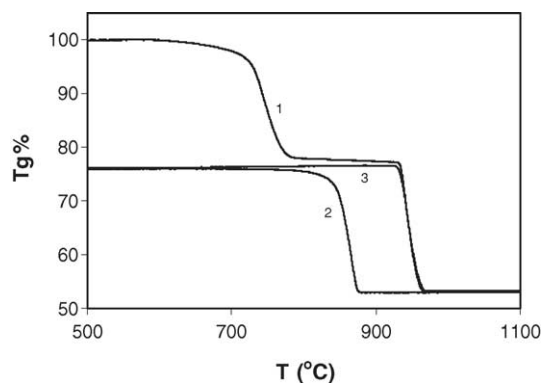


Fig. 1. Calcination/carbonation of dolomitic rocks (sample B-ME3): (1) 1st heating, (2) 1st cooling, and (3) 2nd heating.

3. Results and discussion

The studied samples are presented in Table 1 with their corresponding stoichiometries as it has been inferred by measurements of mass loss [23]. The thermograms of three characteristic samples from Table 1 (B-ME3, BO-PA2, B-SE3) which cover the region from dolomitic rocks up to limestones, are presented in Figs. 1–3. No carbonation of MgO is observed, while the extent of carbonation due to CaO is different for each sample (Table 2). The explicit segregation of the processes of calcinations and carbonation—due to the suffi-

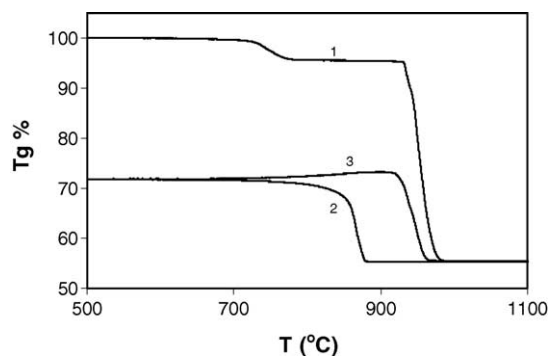


Fig. 2. Calcination/carbonation of dolomitic limestones (sample BO-PA2): (1) 1st heating, (2) 1st cooling, and (3) 2nd heating.

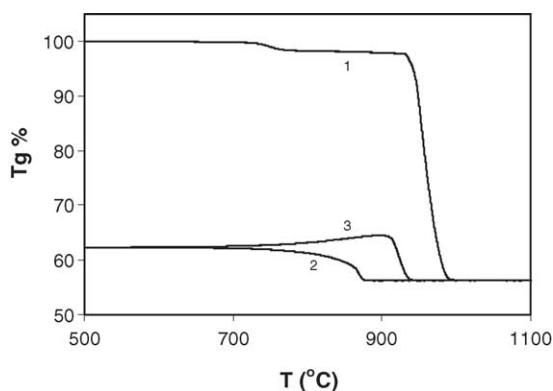


Fig. 3. Calcination/carbonation of limestones (sample B-SE3): (1) 1st heating, (2) 1st cooling and (3) 2nd heating.

cient temperature delay (> 100 C)—allows their corresponding study. In the limestones the total carbonation is not completed in the first step—during cooling—and the process of carbonation is continued at the second heating, completed before the beginning of calcination, while in the dolomitic samples almost the entire carbonation takes place during cooling.

At the first region, it appears that the decrease of the percentage of dolomite results in a decrease in the extent of carbonation, corresponding to a rapid reaction. The diffusion control step, the second region, lasts longer and consequently, the cooling temperature becomes very small eliminating the possibility for carbonation.

For carbonated rocks the surface area and the pore volume of the product increased upon calcination. The dolomitic rocks and the dolomitic limestone provided a higher surface area than the limestone [17]. The calcination/carbonation cycle of dolomitic rocks and dolomitic limestone are depicted in Figs. 1,2. They show that there is a rapid increase in weight in the first minutes during cooling. Once the fractional extent of conversion (α) reaches about 70%, it starts to increase very slowly with temperature (Fig. 4). Initially, the CO_2 diffuses into the narrow pores of CaO and the reaction takes place on the surface area provided by the pores. However, the structure has a high concentration of micro pores. As time elapses, these pores plug up due to the formation of a higher volume

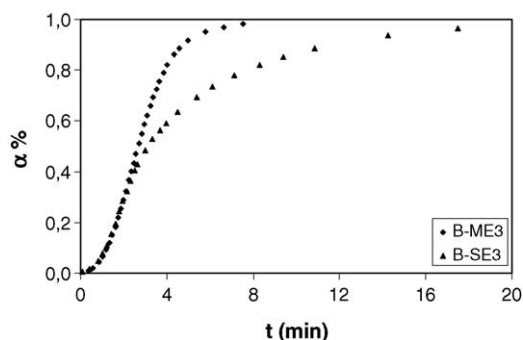


Fig. 4. The dependence of fractional extent of carbonation (α) with time during cooling for two samples (B-ME3, B-SE3).

product of CaCO_3 . Thus the unreacted CaO becomes inaccessible to the CO_2 and this causes a gradual slowdown of the reaction rate [12]. The same trend, as in the case of dolomitic rocks and dolomitic limestone, is also observed for the calcination/carbonation of limestone (Fig. 3). In this case also, there is a sharp increase of conversion initially (about 40%) and then it levels off, as the reaction becomes product layer diffusion controlled (Fig. 4).

The calcination/carbonation of limestone for three complete cycles of heating–cooling of sample B-ER5 is presented in Fig. 5. It is observed that the second cooling coincides in the beginning with the first cooling, but the rate of carbonation is slightly decreased as compared to the first cooling. Also the third cycle of heating–cooling coincides in temperature with the second; however the percentage of carbonation is slightly decreased in the third circle. This reduction is much smaller in the samples with higher percentage of dolomite.

The reversibility of the absorption/desorption process with CaO/ CaCO_3 decreases drastically during the first couple of cycles (Fig. 5). In the cycles following the first two, the influence on the reversibility becomes significantly lower. The absorption capacity decrease can be attributed mainly to the loss of the pores' volume in the oxide and to the sintering of crystallites [4]. The use of structure stabilizing components for CaO, e.g. MgO, can substantially decrease the role of

Table 2

The maximum percentage of carbonated CaO in each sample

	Dolomite (%)	CaO (%)
B-ME3	95.5	96.1
B-ME1	89.6	92.7
K-RY1	89.5	91.6
K-AM1	86.6	91.6
K-AM2	85.8	86.9
BO-PA2	19.4	44.5
B-SE3	7.7	19.6
BO-SX1	2.0	17.7
BO-BI2	1.6	22.6
BO-PR3	1.0	19.1
B-ER5	0.0	35.3
BO-SE3	0.0	13.3

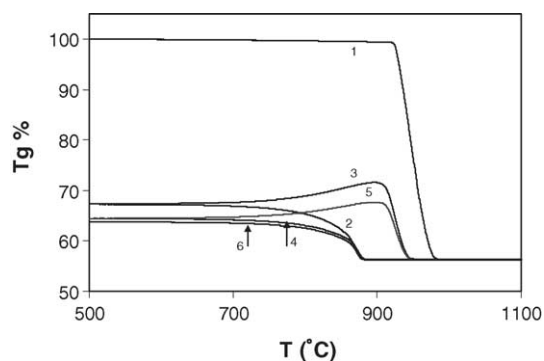


Fig. 5. Variation of the extent of carbonation reaction in 3 cycles of calcination/carbonation for sample B-ER5: (1) 1st cycle-calcination, (2) 1st cycle-carbonation, (3) 2nd cycle-calcination, (4) 2nd cycle-carbonation, (5) 3rd cycle-calcination and (6) 3rd cycle-carbonation.

these effects. The MgO which does not absorb CO₂, has a structure stabilizing effect, giving dolomites a higher cyclic stability compared to calcite.

After the first calcination, the surface area and pore volume increased [15]. Carbonation caused both the surface area and the pore volume to decrease, but not to such small values as the uncalcined dolomite. The second calcination increased the pore volume, to the point of being essentially equal to the pore volume after the first calcination. Also, it restored much of the surface area lost during carbonation. The loss in surface area and the shift to large pore diameters between the first and second calcination cycles are attributed to sintering. Finally, the second carbonation cycle produced the expected decrease, in both surface area and pore volume, to values approximately equal to those following the first carbonation.

A comparison of cyclic stability of different dolomitic rocks, dolomitic limestones and limestone shows the positive effect of the molecular environment on the absorption capacity and cyclic stability. The more inactive material is present in the absorbent, the higher the chemical and thermal stability of the sample it becomes. This is the main effect in the samples in which the percentage of dolomite compared to calcite is important.

Two factors were investigated as for the course of calcination/carbonation of CaCO₃. These are the mass and the cooling and reheating rate. The samples that were used are limestones, because small extent of carbonation was found in this group, in comparison with the other samples. Therefore the study of the different factors in them is of particular interest for their possible industrial exploitation.

In Fig. 6 the carbonation of B-ER5 (1st and 2nd heating) is presented, for two samples of considerably different masses. The surface area which comes in contact with CO₂ during the first calcination is the same for both of them due to the use of the same crucibles. We observe that the extent of calcination for the two samples A and B, having masses 75.4 and 28.8 mg respectively, and the beginning of calcinations, are identical. Small temperature difference between the two different samples is observed, only at the point of completion

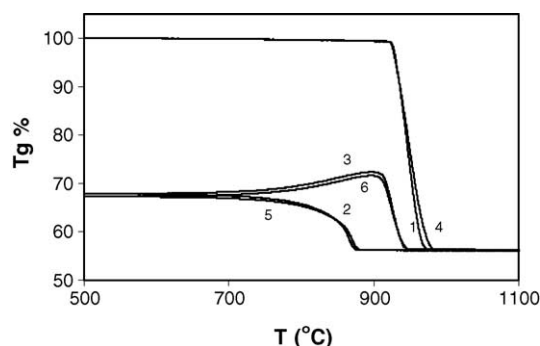


Fig. 6. The dependence of mass on the extent of carbonation reaction for sample B-ER5. Sample A (1) 1st cycle-calcination, (2) 1st cycle-carbonation, (3) 2nd cycle-calcination, sample B (4) 1st cycle-calcination, (5) 1st cycle-carbonation and (6) 2nd cycle-calcination.

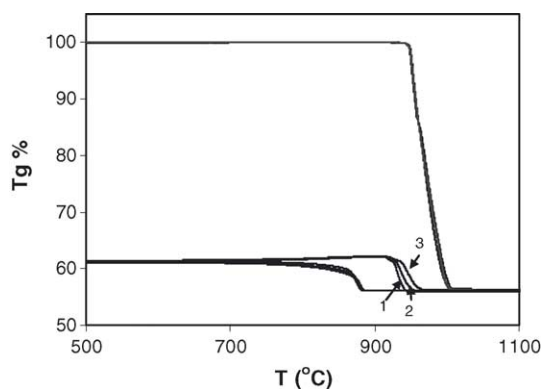


Fig. 7. The dependence of different cooling and reheating rates on the extent of carbonation reaction for sample BO-SE3: (1) rate 10 C/min, (2) rate 5 C/min, (3) rate 2 C/min.

of calcination at the first cycle of heating. In the carbonation reaction, it is observed that the total extent of carbonation in the sample with the smaller mass is a little bigger (0.7%) than that of the other one. This difference is negligible (0.1%) in the sample BO-SE3 and for this reason the corresponding figure is not presented. It is obvious that the mass of the sample affects slightly the extent of carbonation for the group of limestones and the variation of the other limestone samples (B-SE3, BO-BI2, BO-SX1, BO-PR3) ranges between these two. The effect of the heating and the cooling rate in different limestone samples is presented in Fig. 7 and Fig. 8. For each different stoichiometry, were examined three different samples of the same mass which were heated at a rate of 10°/min (first cycle of heating). Then, the samples were cooled and heated again with rates 2, 5, 10°/min. The study of these two variables is focused mainly on the limestone samples, as these samples present low extent of carbonation in relation to the dolomitic rocks where the extent of carbonation reaches almost 100%.

The behavior with the decrease of cooling rate is entirely different for the two presented samples (BO-SE3, BO-BI2). For the sample BO-BI2, the decrease of the cooling rate re-

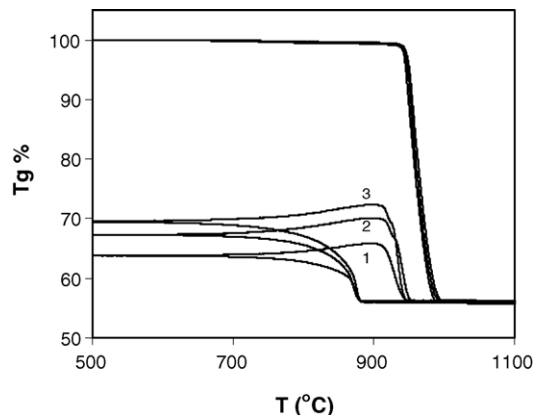


Fig. 8. The dependence of different cooling and reheating rates on the extent of carbonation reaction for sample BO-BI2: (1) rate 10 C/min, (2) rate 5 C/min, and (3) rate 2 C/min.

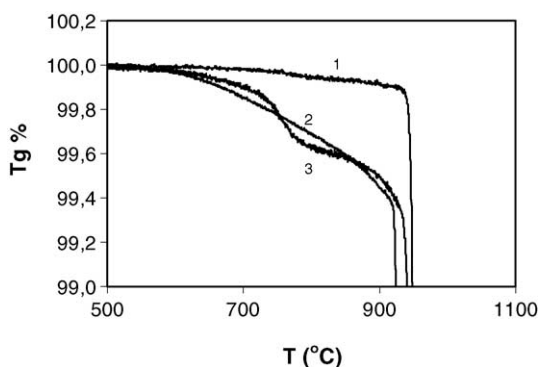


Fig. 9. Early stages of calcinations for three different samples. (1) BO-SE3, (2) B-ER5 and (3) BO-BI2.

sults in the increase of the percentage of CaO which changes to CaCO₃ at cooling (1st cycle) and heating (2nd cycle). The final, however, percentage remains considerably lower than the extent of carbonation in the dolomitic rocks. No differentiation was observed in sample BO-SE3. The behavior of other limestone samples is analogous to the sample BO-BI2.

These observations are useful, particularly in the industrial applications, for the suitable choice of initial material. The interpretation of this different behavior of samples, should be combined with the composition of the samples and the existence of small quantities of dolomite, or impurities or both of them. This diversity is presented in Fig. 9 with the simultaneous presentation of the initial phase of calcination of samples BO-BI2, B-ER5 and BO-SE3. In sample BO-SE3, it appears that the mass loss, in the region of MgCO₃ decomposition, up to the beginning of calcination, is negligible as it occurs in pure calcite. Simultaneously, the calcination is temperature limited. Contrary to the sample BO-SE3, the sample B-ER5 presents an extensive temperature (500–900 °C) monotonous reduction of mass up to the region of CaCO₃ calcination. This does not appear to be, only due to the decomposition of MgCO₃, as on the contrary appears in the sample BO-BI2. According to the literature [24], this temperature extension of the region of decomposition should be attributed to the existence of impurities in the material.

Generally, each replacement of the original cations of a crystal by anions creates physical disorder. Increasing structural disorders (by increasing substitutions) means decreasing bonding energies between the constituents of the crystal structure. This means that increasing crystal chemical disorder lowers the temperature of decomposition. The existence of minimal quantity of dolomite (sample BO-BI2) and dolomite plus impurities, or only impurities (sample B-ER5), appears to be a possible reason for the dependence of the decrease of carbonation on the increase in the cooling and the second heating rate. This could, also, be the reason for the very small differentiation in the extent of carbonation which we observed in the experiments examining the influence of mass.

4. Conclusions

The comparative examination of large group of samples of materials with different stoichiometries of dolomite and calcite, leads to the conclusion that there is a dependence of the extent of carbonation on the presence of dolomite, while it seems to be influenced by the existence of impurities. Furthermore, the cyclability of the reaction is reduced. For the samples having the highest percentage of calcite and the lowest percentage of other elements, the extent of carbonation is not influenced either by the quantity of mass or by the variation of the cooling and the second heating rate. A very small increase in the extent of carbonation was observed in limestone samples with small quantity of dolomite, impurities or a combination of both of them due to the increase in the initial mass of the samples. Also, these samples with the same initial mass presented an increase in the extent of carbonation due to the decrease in the cooling and the second heating rate.

These conclusions are of particular interest for the industrial exploitation of these materials, as at any given time the material of specific composition and specific production conditions can be chosen, which would lead to the reduction of usage cost.

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