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THE EFFECT OF SINTERING ON THE MAXIMUM CAPTURE EFFICIENCY OF CO_2 USING A CARBONATION/CALCINATION CYCLE OF CARBONATE ROCKS

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The effect of sintering on the maximum capture efficiency of CO_2 is studied, using a carbonation/calcination cycle for a series of samples with different stoichiometries of dolomite and calcite. For the materials that belong to the categories of limestone and dolomitic limestone, sintering decreases the extent of carbonation significantly at the two different highest temperatures studied. The extent of carbonation for the same maximum heating temperature depends mainly on the percentage of dolomite. Sintering is negligible in the dolomitic rocks, especially at the maximum heating temperature of 1005°C. The composition of the carrier gas does not seem to play a significant role. The reduction of the extent of carbonation at the second heating /cooling cycle in limestone, and the durability after enough successive cycles of calcination/carbonation in the dolomitic rocks, does not seem to be affected by the maximum temperatures of calcination that were used at the experiments.

Keywords: *carbonated rocks, carbonation, sintering, TG*

Introduction

Solid acceptors for carbon dioxide, used cyclically at high temperatures, have found applications in gas separation and purification, as a source for process heat. The solid acceptors are most often in the form of metal oxides prepared from naturally occurring minerals. Minerals, which have received considerable attention, are limestone and dolomite. Calcium oxide has been proposed as an acceptor for several reactions, including desulfurization, lignite gasification and carbonisation, shift conversion, steam reforming of hydrocarbons, catalytic cracking of hydrocarbon oils and for many other applications [1–8].

The thermal decomposition of dolomite at higher partial pressures of carbon dioxide causes the decomposition to split into a two-stage process [9, 10] as follows:

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \qquad (1)$$

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (2)$$

The reaction-based processes, which were used for separating CO_2 from flue gas, are based on the carbonation in which gaseous CO_2 reacts with solid metal oxide to yield the metal carbonate. Although the thermal decomposition of dolomite, i.e. the second stage that involves the calcination, is usually referred to as a reversible process [11], it is not in fact fully reversible.

The extent of carbonation reported in many studies shows considerable variation [12–22]. 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. Materials with different stoichiometries of dolomite and calcite were not studied. The carrier gas used for carbonation was CO_2, or a combination of CO_2, N_2 and air in various proportions, and for calcination, CO_2 or N_2. 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 and the proportion of the gases of the carrier gas [23]. The extent of carbonation was mainly connected with the pore volume and surface volume of the sorbents.

A factor that affects carbonation is sintering. There is a threshold temperature (Tammann temperature) at which solids begins to present significant sintering. This temperature is 1154°C for calcium oxide, and 533°C for calcium carbonate [12]. According to Pampuch [24], under suitable experimental conditions the sintering temperature is not necessarily coincident with the above mentioned threshold temperature. He determined these temperatures for calcium oxide (900±10°C for 4 micron average diameter) and for magnesium oxide (975±10°C for 4 micron average diameter and 1220±10°C for 14 micron average diameter). In the literature, sintering was studied at different temperatures of isothermal measurements and in various carrier gases, mainly for its influence on the spe-

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cific surface area and on the porosity [25–29]. But there are no quantitative results which connect the effect of sintering with the extent of carbonation, especially in mineral rocks with different stoichiometries of dolomite and calcite. Most of the authors used isothermal measurements to achieve carbonation in low temperatures in order to avoid sintering as much as possible. At these measurements, carbonation needs enough time in order to complete, depending on the initial temperature and other factors that influence the extent of carbonation. But it has not been studied whether this time is sufficient for the appearance of sintering. Probably, the amount of heat that the sample receives at an isothermal experiment is proportional to the amount it would be receiving at a non-isothermal one with a higher final heating temperature.

This article aims to quantify the effect of sintering on the carbonation process in naturally occurring carbonated rocks with different dolomite and calcite stoichiometries. This effect is being studied at two different high heating temperatures. The effect of sintering on the reduction of the extent of carbonation, after continuous cycles of heating and cooling, is also studied.

Experimental

The studied samples were collected from the Kozani broader area (northwestern Macedonia, Greece) [30]. In geotectonic terms, the area belongs to Pelagonian zone. Samples B-SE3 and B-ME3 were collected from carbonate formations of the Vermion Mountain, samples K-RY1 and K-AM2 were collected from carbonate formations near the town of Kozani, samples BO-BI2 and BO-PA2 belong to the quarried limestone formations of Vourinos and sample BO-SE3 belongs to carbonate formations nearby the mountain of Vourinos. The samples B-SE3, BO-BI2 and BO-SE3 are limestones while the B-ME3, K-RY1 and K-AM2 are dolomitic rocks. The sample BO-PA2 is characterized as dolomitic limestone.

Thermogravimetric analysis was made with a Setaram Setsys TG-DTA 1750°C. The samples in powder form with a grain size smaller than 125 μm (measured by sieving) and mass about 40 mg were placed in alumina crucibles. An empty alumina crucible was used as reference. Samples were heated in a 50 mL min^{-1} flow of CO_2. Non-isothermal measurements were used for studying calcination and carbonation. The samples were heated until 1005 or 1200°C and then cooled down to room temperature. At least two complete cycles of heating and cooling were performed for each sample, using the same heating–cooling rate (10°C min^{-1}). For calcium oxide and calcium carbonate, 1200°C is above the Tammann temperature. Also, 1005°C is the lowest temperature we can use, so as for the calcination to be completed in the specific conditions in which the experiments take place.

Results

A series of samples is presented in Table 1 along with their corresponding stoichiometry as it has been calculated by measurements of mass loss [31]. Three characteristic samples from Table 1 (K-AM2, BO-PA2, BO-SE3), which cover the region from dolomitic rocks up to limestone, are presented in Figs 1–3. In each figure the processes of calcination and carbonation (first heating–first cooling–second heating) are presented comparatively for the temperatures of 1005 and 1200°C. A big temperature delay (>100°C) between calcination and carbonation allows the explicit segregation of the two processes and their corresponding study. It appears that the reduction of the percentage of dolomite in limestone results in a decrease in the percentage of carbonation at the first region, which corresponds to a rapid surface reaction. The second region, which corresponds to the diffusion control step, lasts longer. Therefore, the cooling temperature becomes very small so that no possibility for carbonation exists. The first step of carbonation is completed (during cooling) without the achievement of total carbonation for these samples. As a result, the process of carbonation is continued at the second heating, and is completed before the beginning of calcination. We observed the following:

Table 1 Percentage of dolomite and calcite participation in different samples and the maximum percentage of carbonated CaO

	Dolomite/%	Calcite/%	Other/%	CaO/%	
				T_{max} 1200°C	T_{max} 1005°C
B-ME3	95.5	3.9	0.6	96.1	96.4
K-RY1	89.5	10.2	0.3	91.6	94.0
K-AM2	85.8	14.0	0.2	86.9	90.2
BO-PA2	19.4	80.2	0.4	44.5	68.6
B-SE3	7.7	90.8	1.5	19.6	63.0
BO-BI2	1.6	97.9	0.5	22.6	65.8
BO-SE3	0.0	99.8	0.2	13.3	52.3

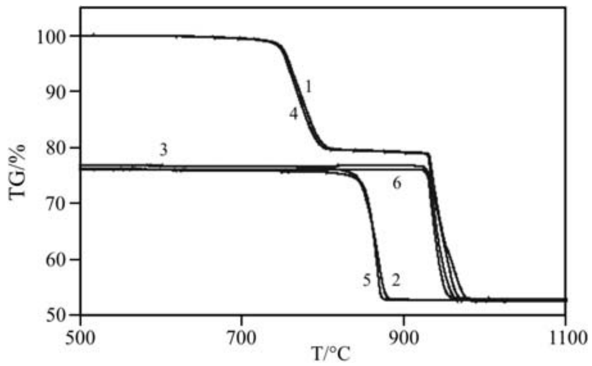

Fig. 1 Calcination/carbonation of dolomitic rocks at different maximum temperatures (sample K-AM2).
1 – 1st heating: T_{max}=1005°C; 2 – 1st cooling: T_{max}=1005°C;
3 – 2nd heating: T_{max}=1005°C; 4 – 1st heating: T_{max}=1200°C;
5 – 1st cooling: T_{max}=1200°C; 6 – 2nd heating: T_{max}=1200°C

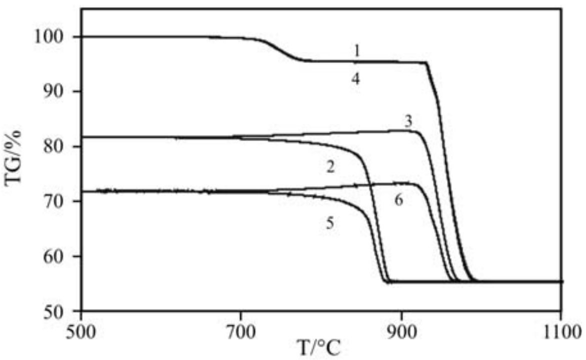

Fig. 2 Calcination/carbonation of dolomitic limestones at different maximum temperatures (sample BO-PA2).
1 – 1st heating: T_{max}=1005°C; 2 – 1st cooling: T_{max}=1005°C;
3 – 2nd heating: T_{max}=1005°C; 4 – 1st heating: T_{max}=1200°C;
5 – 1st cooling: T_{max}=1200°C; 6 – 2nd heating: T_{max}=1200°C

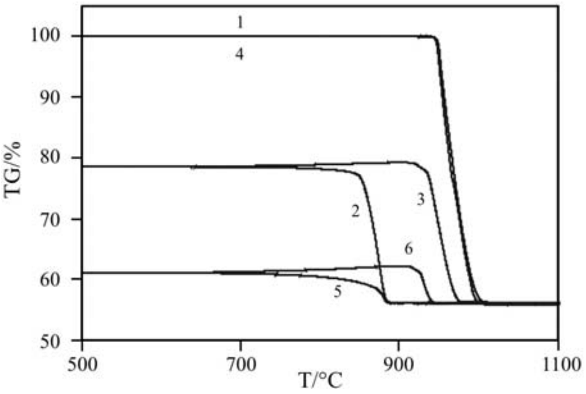

Fig. 3 Calcination/carbonation of limestones at different maximum temperatures (sample BO-SE3).
1 – 1st heating: T_{max}=1005°C; 2 – 1st cooling: T_{max}=1005°C;
3 – 2nd heating: T_{max}=1005°C; 4 – 1st heating: T_{max}=1200°C;
5 – 1st cooling: T_{max}=1200°C; 6 – 2nd heating: T_{max}=1200°C

- During two complete cycles of heating and cooling no change in the mass was seen at temperatures lower than 600°C, for all the samples.
- In samples with even a small quantity of dolomite, it was observed that only calcination is a reversible reaction in the second heating. No mass change was detected at the second heating in the region of the decomposition of $MgCO_3$. However, the percentage of CaO that, during cooling at the first cycle and heating at the second cycle, is carbonated with absorption of CO_2, is different for each sample (Table 1).
- The higher extent of carbonation of CaO is observed during cooling for the samples of limestone, while for the dolomitic samples almost the entire carbonation takes place during cooling (heating–cooling rate is the same for the whole experimental duration).
- For the samples with a high percentage of dolomite, the starting temperature of decomposition is the same at the first and the second heating. For the samples with limited percentage of dolomite (<20%) and T_{max}=1200°C, the decomposition at the second cycle of heating begins and is completed at lower temperatures than the corresponding ones for the first heating. When T_{max}=1005°C, we observe that the temperatures of initiation and completion of calcination at the second heating tend to coincide with those at the first heating as the percentage of dolomite increases in the sample, in a faster rate than in the corresponding samples with T_{max}=1200°C.
- At the second heating, all CO_2 that has been absorbed by CaO abandons the sample. In the end of the second heating, the material has the same mass as in the end of the first heating.
- The decrease in the final heating temperature from 1200 to 1005°C improves significantly the extent of carbonation in the samples with very small percentages of dolomite, while the improvement is minimal and even negligible in samples with very small percentage of calcite (Table 1).

The influence of sintering on the extent of carbonation decrease was also examined for a number of subsequent cycles of heating and cooling. Indicatively we present three subsequent cycles for the sample BO-BI2 (Fig. 4) and 26 cycles for the sample B-ME3 (Fig. 5) at T_{max}=1005°C. Comparing the percentage of carbonation decrease from the first to the second cycle, we observe that this reduction is much smaller for the samples with a higher percentage of dolomite (BO-BI2 19.8%, BO-PA2 15.6%, K-AM2 3%, B-ME3 0.4%). In sample B-ME3 we observe that although the extent of carbonation is negligible during the second heating, as the number of cycles increases the extent of carbonation during heating also increases.

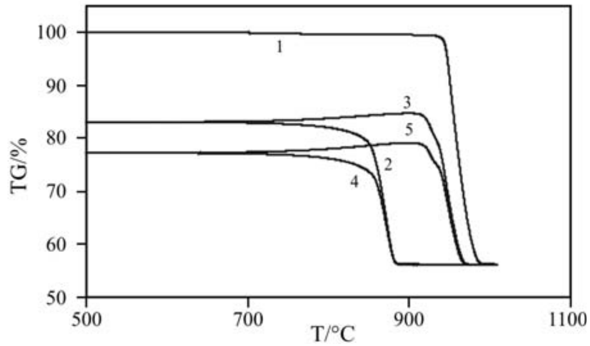

Fig. 4 Variation of the extent of carbonation in three cycles of calcination/carbonation for sample BO-BI2 with $T_{\max}$=1005°C. 1 – 1^{st} calcination, 2 – 1^{st} carbonation, 3 – 2^{nd} calcination, 4 – 2^{nd} carbonation, 5 – 3^{rd} calcination

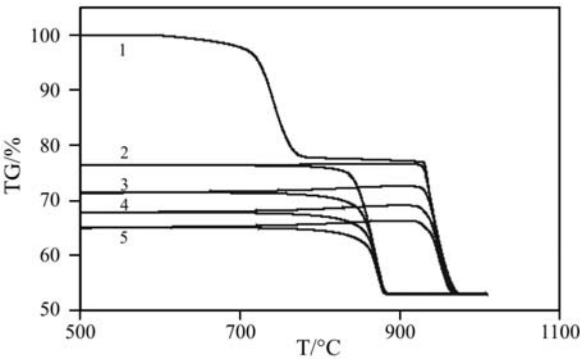

Fig. 5 Variation of the extent of carbonation reaction in twenty-six cycles of calcination/carbonation for sample B-ME3 with $T_{\max}$=1005°C. 1 – 1^{st} heating, 2 – 1^{st} cycle, 3 – 8^{th} cycle, 4 – 17^{th} cycle, 5 – 26^{th} cycle

Discussion

As we know the changes in the surface area and the porosity of the solid, that accompany sintering, can occur at the same time as the reaction of the solid and the fluid (CaO–CO_2). This obviously modifies the reactivity of the solid due to: (*i*) change in surface area and (*ii*) modification in pore size, affecting gas diffusion inside the particle.

For dolomitic rocks, limestone and dolomitic limestone, 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 [15, 23, 28]. In Figs 1–3 and Table 1 we can clearly see the effect of sintering on the extent of carbonation and the differentiation depending on $T_{\max}$. Their different behavior separates the samples into two major groups. The first group includes the samples with small percentage of dolomite (<15%), that is limestone and dolomitic limestone, and the second group the dolomitic rocks. In the first group of materials (limestone and dolomitic limestone), we observe that the increase in the highest temperature from 1005 to 1200°C has a particularly important effect on the reduction of the extent of carbonation. For example, there is a decrease of 75% in the extent of carbonation for the sample BO-SE3. Even if this differentiation is significantly important, the extent of carbonation in these samples is relatively smaller than the one achieved (between 70–80%) under different conditions [18, 28], for example isothermal measurements in lower temperatures (<800°C) and in a carrier gas of different composition (smaller percentage of CO_2). An increase in the extent of carbonation in order to have percentages similar to those of the literature imposes a change of the experiment conditions. This can be succeeded by decreasing the maximum heating temperature with the change of the composition of the carrier gas.

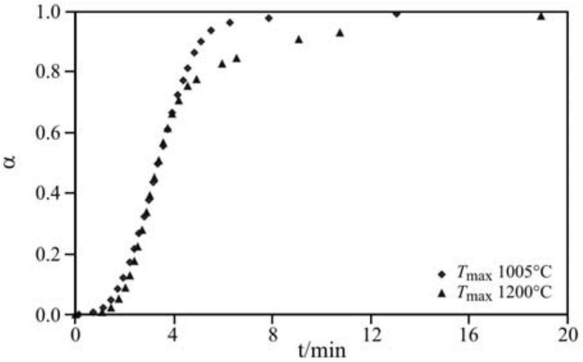

Fig. 6 The dependence of fractional extent of conversion (α) with time for the sample BO-SE3

As we know from the literature [28], in limestone, at the end of the first carbonation the surface area and the pore volume have been decreased. However, only a percentage – which seems to be connected with the maximum heating temperature and the percentage of calcite in the initial limestone of CaO was converted to $CaCO_3$. Rapid initial carbonation followed by an abrupt transition to a slow rate was typical of all experimental tests, as shown in Fig. 6, and consistent with previous reports from the literature [16]. This behaviour can be qualitatively explained on the basis of the changing structural properties of the solid reactant. In principle, pore volume created during calcination should be sufficient to permit complete carbonation of the CaO. In practice, however, carbonation occurs preferentially near the particle exterior so that, as the surface porosity approaches zero, CO_2 is prevented from reaching unreacted CaO at the interior of the particle. Sintering of either or both CaO and $CaCO_3$ may also contribute to pore closure. During the slow reaction phase, either CO_2 must diffuse through a non-porous carbonate layer or CaO must diffuse outward to complete the reaction with CO_2.

According to the literature [26], an increase in the temperature (T>700°C) at which the isothermal process of carbonation takes place, results in the most rapid decrease of the specific surface area and therefore the sintering rate increases as the temperature increases. The duration of the isothermal measurement is the duration of sintering. As shown in Fig. 6 an increase in the maximum temperature leads to a decrease in the carbonation rate, in the area where the fractional extent of conversion is (α)>7. The increase in the sintering rate and the simultaneous decrease in the carbonation rate explain the observed decrease in the extent of carbonation in limestone when the maximum heating temperature increases.

The extent of carbonation for the samples of the second group is equivalent (>90%) to the extent achieved under different conditions, that is isothermal measurements in lower temperatures (<800°C) and different carrier gas composition (smaller percentage of CO_2). Increasing the maximum temperature from 1005 to 1200°C has substantially negligible effect on the reduction of the extent of carbonation (Table 1). Subsequently, in the case of the dolomitic rocks sintering has a minimum effect when the maximum used temperature T_{max} is 1005°C. It also seems that the extent of carbonation is not affected by the experimental conditions, namely non isothermal measurements for calcination and carbonation and carrier gas CO_2. According to the literature, in the case of CaO, the presence of CO_2 as a carrier gas accelerates the sintering process [26]. This different behaviour of dolomite is attributed to the excess pore volume produced during the initial decomposition of $MgCO_3$ and to a reduction in the sintering rate due to MgO. The large pore volume provides improved access of CO_2 to the interior of the particle, which permits increased fractional conversion of CaO to $CaCO_3$. Of the three compounds, $CaCO_3$ has the lowest melting temperature and is, therefore, most prone to sintering [23]. The existence of MgO in some of the samples of the first group, for T_{max}=1200°C, explains the tendency of this group's samples to increase the extent of carbonation, as the percentage of dolomite in them increases. This tendency, finally, is modulated also by the effect, negative or positive, of other constituents which the samples have. When T_{max} becomes 1005°C we observe that this differentiation decreases drastically, a fact which must be connected to the significantly reduced effect of sintering during calcination and carbonation.

Deactivation of acceptors with repeated cycling can take two forms, one of which affects the reaction rate, while the other determines the extent of final conversion. In the cyclic recarbonation (cooling–heating) of calcined dolomite we observe both effects (Fig. 5). The former effect is connected with the increase in the percentage of CaO which, during cooling, does not have the time to be converted to $CaCO_3$. This results in a continuously higher percentage of CaO that is converted to $CaCO_3$ during the heating that is following the cooling. Characteristically, the percentage of CaO that is converted to $CaCO_3$ during heating in the first cycle is hardly 0.9% of the total amount that is converted to $CaCO_3$ during the whole cycle. On the contrary, this percentage increases to 12% during heating in the twenty-sixth cycle. By experiments with limited number of cycles of heating and cooling we find out that in dolomitic rocks, at maximum heating temperature of 1005°C the decrease in the extent of carbonation in the second cycle is very small (0.4–3%) being in accordance with that of the literature [23]. The extent of carbonation in sample B-ME3, which we have succeeded after twenty-six cycles, is the same as the highest extent of carbonation achieved by Dobner [19]. The conditions in his experiments were: isothermal measurement at 700°C and carrier gas of 50% CO_2 and 50% H_2O at atmospheric pressure. Also, the extent of carbonation is higher than the one Silaban uses [23] in his calculations. As we know from the literature [19, 23] dolomite presents more durability in the reduction of the extent of carbonation after successive cycles of calcination/carbonation as compared to calcite. This presents particular interest when we wish to use a cyclic process for the high temperature removal of CO_2 from gases. It is interesting to compare the capacity of two samples, dolomite sample B-ME3 and calcite (results of Silaban [23, 28]). For this we used a capacity index, which is defined on the basis of maximum fractional calcium conversion. From that comparison we have the result that the absolute capacity of dolomite exceeded that of calcium carbonate by the third cycle, while, according to Silaban [23], this was achieved after the fourth cycle. So, we can conclude that sintering at this temperature (1005°C), and under the specific conditions that were used in the experiments, does not seem to play any significant role.

In the group of limestone and dolomitic limestone the reduction of the extent of carbonation from the first to the second cycle seems to be connected to the percentage of the dolomite and the other constituents that exist in the samples. It is in the same value area with samples where carbonation took place in significantly lower temperatures [28].

Conclusions

The use of a group of materials with different dolomite and calcite stoichiometries has given us the possibility of comparative presentation of results in relation to the procedure of carbonation and sintering. The extent of carbonation, for the same maximum temperature, depends mainly on the percentage of dolomite that exists. At the two highest temperatures that we studied, sintering significantly reduces the extent of carbonation for the group of materials that belong to the categories of limestone and dolomitic limestone. The increase in the extent of carbonation in order to have percentages similar to those of the literature, enforces the change of the experimental conditions by decreasing the maximum heating temperature or by changing the composition of the carrier gas by reducing the percentage of CO_2 in it or by combining both parameters. The effect of sintering is negligible for the group of materials that belong to the category of dolomitic rocks, especially for the maximum heating temperature of 1005°C. The composition of the carrier gas does not seem to play any significant role. The reduction of the extent of carbonation in the second cycle does not depend on the sintering and it is equivalent to the percentages of the literature. Furthermore, for the dolomitic rocks the durability in the reduction of the extent of carbonation after successive cycles of calcination/carbonation is equal to or even better than the references of the literature. These conclusions have a particular interest in the industrial exploitation of these materials. Because a material of specific composition and specific production conditions can be chosen at any given time and this will lead to a reduction of usage cost.

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