Thermal decomposition study of crystalline limestone using P-wave velocity

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Abstract

A high-calcium limestone was calcined in order to study its thermal decomposition using P-wave velocity. The onset of calcination is at approximately 750 °C, while its completion according to the size of the cubic specimens is noted between 1000 and 1150 °C. We found that P-wave velocities are a very good index for the study and estimation of calcination. P-wave velocity decreases due to a temperature rise from 650 to 1150 °C for the cubic specimens of 4, 6 and 8 cm mean edge, while for 1 and 2 cm cubic specimens mixed behavior is observed, with a considerable increase in velocities at calcination temperature higher than 1050 °C.

Keywords: Limestone; P-wave velocity; Thermal decomposition

1. Introduction

The main chemical property of limestone is its thermal decomposition, known as "calcination", during which quicklime (CaO) and carbon dioxide are produced. It is a reaction that is strongly affected by the partial pressure of the gas phase (PCO2). An increase in PCO2 partial pressure leads to a rise in the initial calcination temperature [1,2]. According to Boynton [1] CaCO3 decomposition temperature determined by several researchers at the beginning of the 20th century are generally still accepted as 898 °C at 1 atm in a 100% CO2 environment. However, according to some studies, this temperature is set at 902.5 °C [3–5].

The thermal decomposition of MgCO3 (magnesite) is performed at much lower temperatures between 402 and 550 °C depending on the CO2 partial pressure [1,6,7]. Since the MgCO3/CaCO3 ratio varies with the type of limestone, the decomposition temperature does not remain constant and therefore must be determined for every type of limestone. Moreover, differences in the crystallinity of the limestone seem to consolidate the discordance of data. The decomposition of MgCO3 of dolomite is performed at higher temperatures than magnesite. A complete decomposition average value of a high-crystallinity dolomite at 1 atm pressure and 100% CO2 environment is set at 800 °C [1]. The CaCO3 of dolomite resists at higher temperatures, resulting in two decomposition stages.

The aim of this study is to examine the calcination process using P-wave velocity of cubic specimens of several sizes from specific crystalline limestone subjected to calcination experiments under various temperature conditions and retention times.

2. Materials and methods

Cubic specimens of 1, 2, 4, 6 and 8 cm mean edge were prepared from crystalline limestones collected in
the area of Agios Panteleimonas in Florina (NW Greece). More specifically, 72 cubes of 1 cm mean edge (average value 1.14 ± 0.06 cm), 71 cubes of 2 cm mean edge (average value 2.01 ± 0.09 cm), 56 cubes of 4 cm mean edge (average value 4.08 ± 0.13 cm), 56 cubes of 6 cm mean edge (average value 6.19 ± 0.16 cm) and 43 cubes of 8 cm mean edge (average value 8.07 ± 0.27 cm) were prepared. All 298 cubes of approximately 101 kg total weight were calcinated.

According to Kantiranis [8] the average size of the maximum dimension of the studied limestones’ calcite grains is 0.9 mm, their texture is holocrystalline, and by the XRD estimation of their mineralogical composition, it was found that they are very pure, with an average calcite content of 98%. Furthermore, they contain dolomite as well as traces of micas, quartz, chlorite, feldspars, hematite, amphiboles, epidote, pyrite, titanite, ilmenite and zircon. The organic matter is measured at average value of 0.8%, while the insoluble residue of 1.0%.

The experimental calcination was performed at temperatures of 650, 750, 850, 950, 1050 and 1150 °C. Retention times (i.e., the time at which limestone fragments remained inside the kiln at the calcination temperature) for every temperature were 60, 120 and 180 min and the preheating rate was 5 °C/min in all cases. The calcination experiments were performed in a Naber–Multitherm N11/HR furnace ($t_{\text{max}}$: 1260 °C, ±2 °C). All specimens have been weighed before and after their ignition and the difference expressed as a percentage (wt%) is the ignition loss for every calcination condition.

The calculation of compression wave (P-wave) velocity passing through a material was conducted according to the French standard AFNOR NF B 10505 [9]. Measurements were made using a PUNDIT velocimeter taking into account every dimension (X, Y, Z) of the specimen. Special uniplanar transducers (see Fig. 1) are adjusted to the polar edges of the specimen, while for the measurement of P-wave traveling times in this study 54 kHz transducers were used. According to the ASTM C597 [10] for specimens with short path lengths (50 mm or shorter), where the loss of signal is not the governing factor, it is preferable to use vibrational frequencies of 50 kHz or higher to achieve more accurate transit-time measurements and hence greater sensitivity. By dividing the specimens’ length (traveling distance of P-waves) by the traveling times, we are able to estimate the velocity of P-waves through the cubic specimens. In order to improve the acoustic contact between the specimen and the transducers, yellow plasticine was used as a contact agent, while for the accurate adjustment of the device was equipped with a cylindrical aluminum alloy template (Fig. 1). According to Lemoni [11] plasticine slightly affects the P-wave velocity and the measurements that are received are particularly reliable comparatively with other contact agents, such as aluminium plates, vaseline, grease, soft soap, etc. The calcined specimens were cooled in a dehumidifier and then were measured at ambient temperature.

The ultrasonic technique for the estimation of calcination was applied experimentally for the first time by Kantiranis [12] and showed [12,13], that it is a very useful and reliable technique for the study of calcination of a carbonate rock. P-wave velocity is a very good index for the quality of rocks and other materials (e.g., mortars) [14–19].

### 3. Results and discussion

In Table 1 the average P-wave velocity (3 readings/specimen × 298 specimens = 894 readings), its SD and the average loss of ignition of the samples studied were given. The correlation of the loss of ignition with the
calcination temperatures is presented in Fig. 2. The sigmoidal or Boltzmann distribution was used for the correlation of the data according to the following formula:

\[ y = \frac{A_1 - A_2}{1 + e^{\frac{x}{x_0}}} + A_2, \]

where \( y \) represents the loss of ignition (wt%), \( x \) is the calcination temperature (°C) and \( A_1, A_2, x_0, d_0 \) are the Boltzmann constants. According to Table 1 and Fig. 2 the onset of calcination is at approximately 750 °C (average loss of ignition >1%). The completion of calcination, depending on the size of cubic specimens, is noted between 1000 and 1150 °C. The cubic specimens of 1 cm mean edge are completely calcined at approximately 1000 °C for retention times longer than 120 min, while the cubic specimens of 8 cm mean edge at 1150 °C even for retention times of 60 min. For the other specimen sizes, the completion of calcination is observed at intermediate conditions. For cubic specimens of the same edge, calcination at a specific temperature depends strongly on retention time. Extended retention times lead to lower temperatures of complete calcination. Ruckensteiner et al. [20] studied different limestones and found that their calcination begins at 520 °C and it is completed at 895 °C. Kantiranis [12] and Kantiranis et al. [13] studied cubic specimens of 5 cm mean edge from crystalline limestones of Agios Panteleimonas in Florina and found that their calcination begins at approximately 740 °C.

On the initial cubic specimens of the studied limestone 801 measurements of P-wave velocity at ambient temperature in all cubic directions were conducted before the calcination. An average value of 5518 m/s with SD 475 m/s was found, with a minimum value of 3643 m/s and maximum value of 6427 m/s, while no any specimen size effect was observed. P-wave velocity in limestones ranges between 3500 and 6500 m/s [21], while for a calcite crystal the P-wave velocity is 6490 m/s [22].

The correlation of P-wave velocity (m/s) with the calcination temperature (°C) is presented in Fig. 3. For this correlation the third grade polynomial distribution was used. Based on Table 1 and Fig. 3, the average P-wave velocity decreases due to temperature rise for the cubic specimens of 4, 6 and 8 cm mean edge and ranges from 2248 to 753 m/s. Especially for the cubic specimens of 8 cm mean edge, this transition is very smooth. The cubic specimens of 1 and 2 cm mean edge present a more complex behavior and, more specifically, up to 1050 °C, P-wave velocity decreases to 745 m/s. The velocity then increases due to an increase of the retention time at calcination temperatures higher than 1050 °C. This phenomenon is intense in the case study of the calcination of the 1 cm specimens especially at 1150 °C for a retention time of 180 min, during which an average P-wave velocity of 2045 m/s was measured. This increase may be related only to a decrease in porosity and an increase in the dry apparent weight representing the shrinkage of the produced quicklime [8].

According to Rubiera et al. [23] and Wong and Brandt [24], during completion of calcination the textural characteristics of the calcinated specimens are constantly changing due to contraction and shrinkage phenomena. The shrinkage phenomena and the density growth are due to the fact that the CaO molecular crystals formed by the thermal decomposition of CaCO₃ are united at the same time into gradually bigger crystals, the “crystallites”. In a pure calcite at 900 °C these crystals are only approximately 0.1 μm in size, and at
1000 °C they are 1 μm in size, due to the symphysis of these crystallites. At 1100 °C an even bigger agglomeration of crystallites is formed turning constantly into a more compact mass relative to the temperature rise [25].

Also, an important point is that at an ignition temperature of 650 °C and retention time 60 min and despite the absence of calcination phenomena, a considerable decrease in P-wave velocity is noted from an average value of 5518 to 2124 m/s. This behavior is probably related to the structural changes of the limestone during heating. The expansion/contraction of calcite crystals, but also the combustion of the organic material that a limestone may contain leaving microscopic holes that decrease P-wave velocity [1,2,13].

In coarse grain crystalline limestones the instability phenomena of their fragments and fragmentation are due to the different thermal expansion coefficient of the large calcite crystals horizontal \((25 \times 10^{-6} \text{ K}^{-1})\) and vertical \((5 \times 10^{-6} \text{ K}^{-1})\) to the c axis. Limestones intersected by a dense vein system empty or filled with...
sparitic calcite are highly susceptible to fragmentation [20]. P-wave velocity, as a natural characteristic of rocks and different materials, depends on their micro- and macro-structure, the existence of minor cracks and porosity and the characteristics of their mineralogical components, such as elastic parameters, density and microporosity [22]. Increased velocity with an increase in the dry apparent weight and vice versa is reported by Babuška [26] and Kopf et al. [27]. The effect of minor cracks on the distribution of P-wave velocity in rocks has been studied by Babuška et al. [28] and Jech et al. [29]. The P-wave velocity of a rock decreases with the growth of the average size of grains [22].

Based on the study of P-wave velocity, it is concluded that it depends directly on the calcination temperature and, consequently, the loss of ignition. More specifically (Table 2), a decrease by approximately 61% (5.4 m/s/°C) is observed between the average value of P-wave velocity in the initial material and at the milder ignition temperature (650 °C). As temperature rises to 750 °C and to 850 °C, almost the same decrease in P-wave velocity is observed at approximately 15% (3.2 m/s/°C) and 18% (3.3 m/s/°C), respectively. On the contrary, at temperatures of 950 °C, where according to the literature the thermal decomposition of calcite is completed, a more considerable decrease in P-wave velocity is observed of 23% (3.5 m/s/°C). At higher temperature of 1050 °C, where the calcination of most specimens of the studied limestone is completed, a decrease of 22% (2.6 m/s/°C) in P-wave velocity is noted. Finally, at the highest temperature (1150°C) P-wave velocities show a mixed behavior. For the cubic samples of 1 and 2 cm mean edge an increase of P-wave velocity is observed, with an average value of 58% and 7%, respectively. This increase probably indicating the contraction and/or shrinkage of the specimens. Almost the same average P-wave velocity is determined for the cubic samples of 4 cm mean edge at temperatures 1050 and 1150 °C,

Fig. 3. Correlation of the average P-wave velocity (m/s) vs calcination temperature (°C) (R² correlation coefficient).
Table 2

<table>
<thead>
<tr>
<th>Calcination temperature (°C)</th>
<th>Cubic samples with mean edge</th>
<th>Mean value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 cm</td>
<td>2 cm</td>
</tr>
<tr>
<td>Initial material → 650</td>
<td>−61</td>
<td>−61</td>
</tr>
<tr>
<td>650 → 750</td>
<td>−14</td>
<td>−13</td>
</tr>
<tr>
<td>750 → 850</td>
<td>−17</td>
<td>−16</td>
</tr>
<tr>
<td>850 → 950</td>
<td>−30</td>
<td>−20</td>
</tr>
<tr>
<td>950 → 1050</td>
<td>−15</td>
<td>−37</td>
</tr>
<tr>
<td>1050 → 1150</td>
<td>+58</td>
<td>+7</td>
</tr>
</tbody>
</table>

→, Decrease of velocity; +, increase of velocity.

while a decrease is observed, with an average value of 13% and 18% for the cubic samples of 6 and 8 cm mean edge, respectively.

Timur [30] has examined the variation of ultrasonic velocity in relation to temperature in specimens of sedimentary rocks maintaining the external and internal pressure constants. He found that P-wave velocity shows a linear decrease with temperature up to 200 °C. According to Toksoz et al. [31], an important factor affecting the decrease of P-wave velocity, apart from the dry apparent weight, is the creation of micro-cracks. These micro-cracks are created due to anisotropic thermal expansion of the material inside the cracks, in relation to the matrix, when a rock contains secondary veins.

4. Conclusions

The onset of calcination is at approximately 750 °C, while its completion according to the size of the cubic specimens is noted at between 1000 and 1150 °C. For similar sizes of cubic specimens, complete calcination at a specific temperature depends on the retention time at this temperature. Extended retention times lead to lower temperatures of complete calcination.

We found that P-wave velocities are a very good index for the study and estimation of calcination. More specifically, P-wave velocity decreases due to a temperature rise for the cubic specimens of 4, 6 and 8 cm mean edge, while for 1 and 2 cm cubic specimens mixed behavior is observed, with a considerable increase in velocities at calcination temperatures higher than 1050 °C.

A decrease of approximately 61% (5.4 m/s/°C) in the P-wave velocity at 650 °C compared to its value in the initial material was observed. As temperature rises to 750 °C and to 850 °C, almost the same decrease in P-wave velocity is observed of 15% (3.2 m/s/°C) and 18% (3.3 m/s/°C), respectively. At temperature of 950 °C, a more considerable decrease in P-wave velocity of 23% (3.5 m/s/°C) is observed. At higher temperature of 1050 °C, a decrease of 22% (2.6 m/s/°C) in the P-wave velocity is observed. Finally, at the highest temperature (1150 °C) P-wave velocities show a mixed behavior. For the cubic samples of 1 and 2 cm mean edge an increase of P-wave velocity is observed, with an average value of 58% and 7%, respectively. This increase probably indicating the contraction and/or shrinkage of the specimens. Almost the same P-wave velocity is determined for the cubic samples of 4 cm mean edge at temperatures 1050 and 1150 °C, while a decrease is observed, with an average value of 13% and 18% for the cubic samples of 6 and 8 cm mean edge, respectively.

Studying samples during and after the process of calcination at lime kiln by ultrasonic technique in the lime industry, could be a useful tool for the evaluation of the calcination process in industrial scale. Phenomena of incomplete calcination that are caused by soft conditions of calcination (small retention time and/or low temperature), as well as phenomena of hard burning that are owed in extended retention at high temperatures of calcination leading to constriction of the limestone fragments and finally to the reduction of the reactivity of the produced lime, can very easily be determined with the use of this non destructive, practical and rapid method.

References


