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APPLICATION OF ULTRASONIC VELOCITY MEASUREMENT AND THERMAL ANALYSIS FOR DETERMINATION OF LIMESTONE QUALITY

Ozen KILIC

Department of Mining Engineering, Faculty of Engineering-Architecture, University of Cukurova, Balcali-Adana, 01330, Turkey, zenkilic@cu.edu.tr

Abstract: Limestone is an important industrial raw material. It is consumed by chemical and other industries (84%), used as refractory and road construction material (12%) and applied in civil engineering and agricultural applications (4%). Substantial amounts of limestone are also used as lime in the iron and steel industry. The aim of this study was to determine the properties of limestones. The chemical, physical and thermal properties of limestones were determined by standard methods while the P-wave velocities of limestones were measured with an ultrasonic non-destructive tester and relationships between limestone properties were estimated. It was found that there is a statistical correlation between physical properties and the P-wave velocity of limestones. The P-wave velocity is a very good characteristic parameter for the study and estimation of the limestone quality.

Keywords: *limestone properties, thermal decomposition, TG-DTA, P-wave velocity*

Introduction

In broadest definition, limestone is any rock rich in $CaCO_3$. Limestone can be obtained from a variety of sources and various limestones differ considerably in their chemical compositions and physical structure. The chemical and physical properties of carbonate rocks are interdependent. Physical characteristics of limestone play an important role in evaluation of a deposit. Certain physical characteristics of limestones may indicate the general susceptibility to decrepitation during calcination; however, not all stones with these characteristics will decrepitate. Limestones that display the following attributes or conditions, alone or in combination, are prone to decrepitation; coarse crystallinity, friability, foliation, excessive calcite veining, microfracturing, highly porous and thin-bedded structure. The chemical reactivity of different limestones shows a large variation due to their differences in crystalline structure and the nature of impurities such as silica, iron, magnesium, manganese, sodium, and

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potassium. Magnesium and ferrous iron cations occurring in limestone may change the carbonate mineralogy of limestone as well as its physical characteristics such as color, brightness, specific gravity, hardness, tenacity and decomposition properties (Boynton, 1980; Krukowski, 2006).

The main chemical property of limestone is its susceptibility to thermal decomposition, known as calcination, during which lime (CaO) and carbon dioxide are produced (Eq. 1) (Boynton, 1980; Oates, 1998).

The calcination reaction is endothermic

$$CaCO_3 \rightarrow CaO + CO_2 \quad \Delta H = 182.1 \text{ kJ mol}^{-1} \tag{1}$$

which means that the forward reaction is favored by higher temperatures. The reaction will proceed only if the partial pressure of CO_2 in the gas above the solid surface is less than the decomposition pressure of the $CaCO_3$. The latter pressure is determined by equilibrium thermodynamic considerations (Coats and Redfern, 1964).

The reaction (Eq.1) begins only when the temperature is above the dissociation temperature of the carbonates in the limestone. According to Boynton (1980), the $CaCO_3$ decomposition temperature determined by several researchers at the beginning of the 20th century is generally still accepted as 898 ºC at 1 atm in a 100% CO_2 environment. However, according to some studies, this temperature is 902.5 °C (Turkdogan et al., 1973; Thompson, 1979; Borgwardt, 1985). Kilic (2005) is reported that the weight loss above 600 °C, measured by DTA-TG in nitrogen atmosphere is attributed to CO_2 from the decomposition of calcium carbonate that is initiated at 682-691°C and completed at 944-961 °C.

The internal structure of a rock having open and closed pores in its texture affects the heat transfer. The specimen comprises a dense carbonate core surrounded by porous oxide layer. The changes in pore structure also play a significant role in the calcination/heat treatment mechanism and the reactivity of a calcined limestone strongly depends on its chemical, physical and structural properties, which in turn are highly dependent on heat treatment conditions (Rubiera et al., 1991; Khinast et al., 1996). In the good calcination process, limestone should consist approximately 97% of $CaCO_3$ and contain little impurities. Impurities such as iron, magnesium and aluminum oxides lead to lower surface areas in both the limestones and their calcines (Trikkel and Kuusik, 2003).

Ultrasonic techniques have been used for many years in geotechnical practice and mining science. They are employed in the field of geophysical investigations and in the laboratory for the determination of the dynamic properties of rocks. Since these techniques are non destructive and easy to apply, they have increasingly been used. Most researchers (Timur 1977; Parasnis, 1997; Vajdova et al., 1999; Kilic, 2006) studied the relations between rock properties and sound velocity and found that it is closely related with the rock properties. P-wave velocity is a very good index for the quality of rocks and other materials (e.g., mortars, lime quality).

The current demand of limestone worldwide has necessitated investigation of the limestone quality regarding the limestone chemical composition, physical properties and thermal properties. The aim of this study is to examine the properties of the limestone by standard test methods and to estimate these properties using the Pundit instrument, i.e. by an indirect method. The determination methods of chemical and physical and thermal properties of limestones are highly time-consuming and costly methods.

Materials and methods

The limestones were taken from different large commercial deposits: Karaisali region (L_k) and Yılankale region (L_y) in Adana, Turkey. During sampling, rock types having no bedding planes were selected to eliminate any anisotropic effects in the measurements of the samples. Limestones present macroscopically different characteristics. L_k is a 'dirty white' and light coloured grey limestone comprising discrete and tiny crystals. L_y is light-coloured 'dirty white' without any distinguished crystals. Microcracks were not present throughout the mass of L_k limestones, but microcracks, dense vein system and schistosity were observed throughout the mass of L_y limestones.

Analytical methods and techniques

Analyses were performed on limestone samples by using the following analytical procedure.

- XRF (Siemens SRS 300 X-ray Fluorescence Spectrometer) was used to determine the chemical compositions of limestone samples.
- X-ray diffraction (XRD) analyses of finely pulverized limestone samples for the identification of the presented crystalline compounds were performed with a Rigaku Minflex 2. The diffraction angle (2θ) interval was 20°–60° with a step of 0.02°.
- Physical properties (the bulk density, effective porosity, water absorption rate) of the limestones were determined using saturation and buoyancy techniques, as recommended by ISRM and TSE (TS EN 1097-2, 2010).
- P-wave velocities were measured by the Pundit instrument (CNS Farnel Pundit Plus C-Portable Ultrasonic Non-Destructive Indicator Tester), which has two transducers (a transmitter and a receiver) having a frequency of 54 kHz.
- Differential thermal and thermogravimetric analyses (simultaneous TG/DTA, Setaram 92 16 DTA-TG) were carried out to determine quantitatively and qualitatively the various compounds presented in samples. Analyses were performed in samples of limestone in nitrogen atmosphere in the temperature range of 25–1000 °C and gradient of 10 °C/min.

Results and discussion

The chemical analyses results of limestone samples are presented in Table 1. It was found that the studied limestones are very pure with an average $CaCO_3$ content higher than 97%. The impurities concentrations (MgO, Fe_2O_3, Al_2O_3 and SiO_2) are very low. Since the $MgCO_3/CaCO_3$ ratio varies with the type of limestone, the decomposition temperature does not remain constant and therefore must be determined for every type of limestone.

The mineralogical analysis of the limestones (L_y and L_k) was done by XRD analysis technique. It was found that they were very pure and calcite was the main component in both samples, with little quartz.

Table 1. Chemical compositions of limestone (%)

Sample	CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	Loss on Ignition
L_k	55.13±0.14	0.44±0.04	0.34±0.22	0.08±0.04	0.07±0.03	43.95±0.15
L_y	54.90±0.35	0.74±0.58	0.55±0.31	0.10±0.05	0.08±0.06	43.63±0.53

The physical properties results of limestones are presented in Table 2. All limestone samples indicated low values of porosity and water absorption rate (lower than 1%). The value of apparent density (>2.55 g/cm^3) was found to be characteristic for a limestone (Stanmore and Gilot, 2005). Comparing the limestones, L_y demonstrated higher values in porosity.

The physical properties depend not only on the properties of the individual minerals, but also upon the way in which the minerals are assembled and porosity, vein system and micro-cracks. The relevant information is given by P-wave velocities, which includes the pores and cracks. Information on the porous nature of rock materials is frequently omitted from physical descriptions, but is required if these descriptions are to be used as a guide to mechanical performance (Smorodinov et al., 1970). Bulk density is relevant to chemical composition of the limestone. Bulk density increases with the increase in $MgCO_3$ content.

P wave velocity was used to determine the changes in the physical properties of the limestone samples. P-wave velocity measurements may be performed by the direct method at room conditions through ultrasonic pulse transmission technique by the Pundit instrument (Fig. 1). Velocity measurements were carried out on the cubic specimens. The test was repeated three times in three perpendicular directions and the mean values were recorded as the P-wave velocity.

The P-wave velocity in the limestones ranges between 3.500 and 6.500 km/s (Parasnis, 1997) while, for a calcite crystal, the P-wave velocity is 6.490 km/s (Vajdova et al., 1999). In the tests, the P-wave velocity in L_k and L_y was measured as 5.701±0.044 and 5.635±0.051 km/s, respectively (Table 2). The P-wave velocity measurement values have showed that all specimens have minor cracks and porosity.

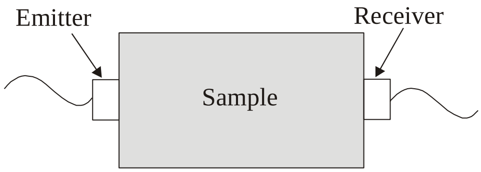

Fig. 1. The method of measuring P-wave velocity

Table 2. Physical properties of the limestones

Sample	Bulk density (g/cm^3)	Water absorption rate (weight) (%)	Porosity (%)	P-wave velocities (km/s)
L_k	2.65±0.08	0.62±0.12	0.75±0.08	5.701±0.044
L_y	2.66±0.14	0.79±0.19	0.85±0.16	5.635±0.051

The 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 micro-porosity (Vajdova et al., 1999). Increased velocity with an increase in the dry apparent weight and vice versa is reported by Babuska (1968) and Kopf et al. (1985).

According to Toksoz et al. (1976), 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.

The graphs (Figs. 2–4) of the P-wave velocity versus bulk density and porosity have been presented for L_k and L_y. Among the relations, bulk density (Fig. 2), water absorption rate (Fig. 3) and porosity (Fig. 4) against P-wave velocity have a correlation R^2 = 0.9862, R^2 = 0.9812 and 0.9875, respectively. Strong statistical correlation between physical properties and P wave velocity were found.

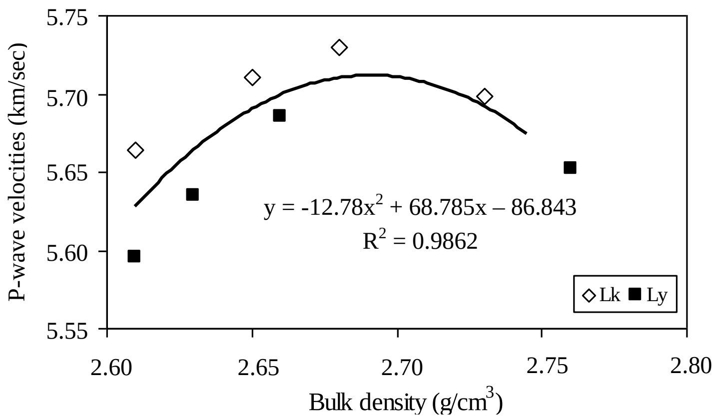

Fig. 2. Correlation of P-wave velocity vs. bulk density

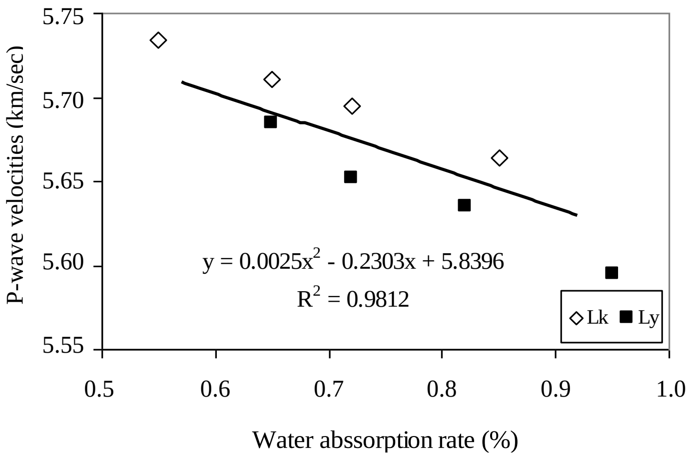

Fig. 3. Correlation of P-wave velocity vs. water absorption rate

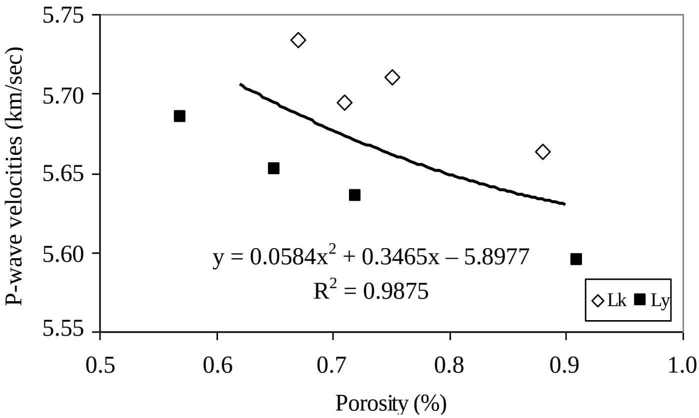

Fig. 4. Correlation of P-wave velocity vs. porosity

The differential thermal analysis technique has been used for the quantitative determination of the heats of decomposition of carbonate materials. It is observed that the carbonates; i.e. limestone, dolomite, have lower heats of decomposition and higher energies of activation in a carbon dioxide atmosphere compared to values obtained in air.

The thermal analysis was performed simultaneously by means of TG–DTA. TG and DTA curves (Figs. 5–6) for the limestones L_k and L_y were obtained by continuous heating from room temperature to 1000 °C at a heating rate of 10 ºC/min. The observed changes are attributed to CO_2 from the decomposition of calcium carbonate.

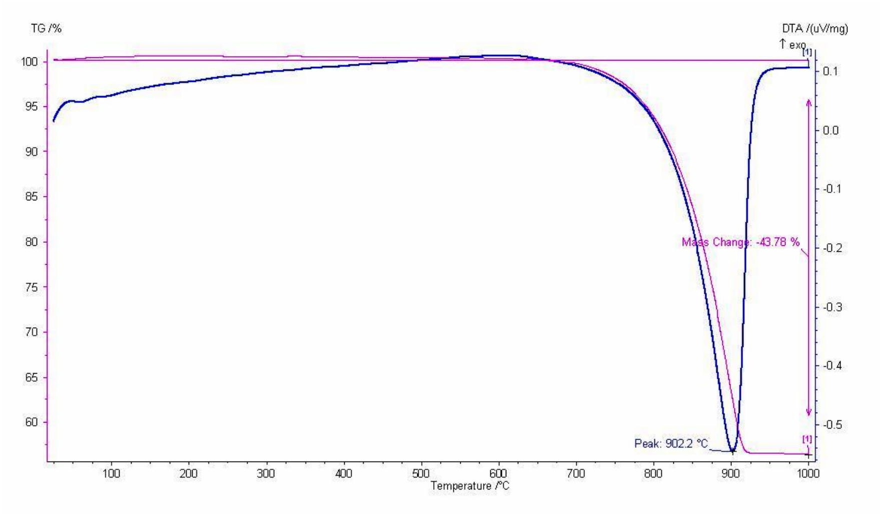

Fig. 5. The TG-DTA curve for L_k decomposition

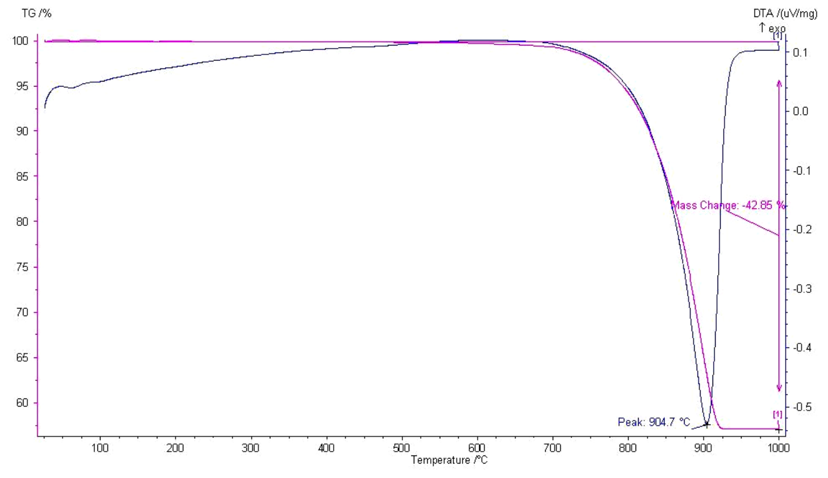

Fig. 6. The TG-DTA curve for L_y decomposition

The figures showed that the weight loss is initiated at 625 and 675 ^{o}C and *e* (eq. (1)) full decomposition ended approximately at 925 and 935 ^{o}C for L_y and L_k, respectively. Comparing the percentage values of CO_2 measured by DTA/TG, it is evident that the values are very high and similar to each other. Thus, the limestones could be characterized as high calcium ones. Furthermore, it is observed that the percentage of CO_2 for limestones is higher than the theoretical one.

In the evaluation of the thermal decomposition of limestone is complicated by the CO_2 presence, which inhibits the reaction; particle size, which may introduce both thermal and mass transfer limitations, and catalysis/inhibition by impurities. When calcination takes place (eq. (1)), the obtained calcium oxide weighs only 56% of the parent carbonate. It was understood that limestones are very pure and main mineral is calcite in both samples because no other endothermic peaks (Figs. 5–6) are observed.

This study also showed that depending on the chemical, petrographic and mechanical features of limestone, before it undergoes calcination it is possible to give an estimation of the quality the produced lime, basing on the conditions and temperature of calcination. Using the measurement of P-wave velocity it is possible to give the estimation of the quality of the limestone without analyses which are costly and takes much time.

Conclusions

The studies aiming to determine the properties of the limestones by standard test methods and estimate these peculiarities via P-wave velocities using the Pundit instruments by indirect method are presented. The relation between limestone properties and the results of P-wave velocity measurements were established.

The analysis showed that the L_k and L_y contain sufficiently high percentages of the calcium oxide and calcite mineral was the main component of the both samples. Since the $MgCO_3/CaCO_3$ ratio varies with the type of limestone the decomposition temperature does not remain constant and therefore must be determined for every type of limestone.

It was found in this study that the unit weight of the limestone is larger than 2.55 g/cm^3 and the samples showed low porosity and low water absorption rate (<%1). These findings show the fact that these limestones have compact texture and this type of stones could be preferred as quality limestone.

The thermal decomposition of limestone depends on chemical composition, physical properties and decomposition temperature of calcium carbonate. The reaction temperature has a direct effect on the conductivity of limestone depending on their impurities, porosity and micro-cracks, and hence on the rate of reaction. The reaction rate can be enhanced through improved heat transfer systems.

Samples with higher %$CaCO_3$ content and P-wave velocity and lower bulk density and porosity show relatively higher activation energy and rate of lime crystallite growth. This is due to the original grain channel pores and the formation of triple junction fractures during decomposition process, which facilitate transfer of hot gases and diffusivity of the evolved CO_2. It is finally concluded that decomposition process of limestone is a temperature, chemical and physical properties dependent process.

These results of the experiments show that limestones (L_k and L_y) have compact texture, low porosity, high CaO and low impurity and good thermal conductivity, this type of stones are preferred in several industry; such as road construction and production of lime.

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