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Technical Note

Thermal effects on the physical properties of limestones from the Yucatan Peninsula

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ABSTRACT

The effect of thermal degradation on the compression strength, ultimate compression strain, color and mass loss of four limestones extracted from the Yucatan Peninsula was studied. The samples sets were independently subjected to 25, 100, 200, 300, 400, 500 and 600 °C during one hour for each temperature. The thermal degradation of the investigated rocks and their chemical composition, microstructure and porosity is also investigated. The results show a correlation between the mechanical properties, thermal behavior, the presence of minerals and porosity in each type of limestone rock. The variation of the limestones color with temperature was described in terms of standard space color parameters and their diffuse reflectance.

1. Introduction

The historical monuments and archeological sites in the Maya area comprising southern Mexico, the central part of Honduras and Guatemala, are constructed with different types of limestone, with calcium carbonates ($CaCO_3$) as the basic constituent. Currently in the Yucatan Peninsula there are a variety of historical constructions and archeological sites built with stones. The Peninsula of Yucatan is a smooth carbonate platform developed from Cretaceous, Tertiary and Quaternary limestones, with predominantly shallow calcareous soil [1], containing different grain sizes, porosities, and texture. Also, many modern buildings use limestone as a primary construction material.

Limestones can be obtained from a variety of sources and may differ considerably in their chemical compositions and physical microstructure. The chemical reactivity show a large variation due to their differences in crystalline structure and the nature of impurities (silica, iron, magnesium, manganese, sodium, and potassium, to name a few) [2].

The study of changes in the physical properties of rocks as a function of thermal excursions is relevant to various engineering and industrial applications. Rocks are composed of minerals, bounding matrix, cracks and pores, and heat may produces important physical and chemical changes in their microstructure [3]. Temperature changes can induce micro-cracks in the rocks due to the mismatch in the thermal properties of the different mineral compositions (intergranular) or within grains (intragranular) [4]. Temperature gradients can affect the rock dilation, changing the coefficients of thermal expansion [5]. Qualitative changes produced by heat can also occur when the rocks undergo a phase transition such as the α/β phase transition in quartz [6].

One of the traditional forms of tropical agriculture in the Yucatan peninsula is the "slash-and-burn" system that is applied every year, during the dry periods [7,8]. Temperature measurements on these traditional practices can reach non-uniform high temperatures from 300 °C up to 700 °C [9]. These repeated burnings and extreme heating changes can lead to long term cumulative thermal effects on the rock properties and ecosystem. This is because the modifications of the mechanical properties of limestones have a strong influence on the soil conformation and induce erosion, promoting water infiltration, increased permeability and porosity, which are one of the major problems in these regions.

Temperature variations are one of the major factors influencing the intrinsic properties of rocks [10,11]. It has been shown that the variation of expansion increases with temperature [3], which is primarily responsible for the changes in the microstructure of rocks, inducing new fractures and microfractures. A common form of chemical action caused by temperature is the oxidation of iron, which provokes significant color changes even in the presence of minor amounts of iron (ferrous minerals) in the calcareous matrix. For example, red coloration is due to the presence of hematite, whereas less common yellows and browns generally result from

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limonite and goethite, respectively. The green-gray to black color in rocks is related to total organic carbon where darker colors corresponding to higher carbon content; this relationship has been confirmed on sediments [12]. The presence of kaolinite and smectite provide white to light neutral colors. Compounds of other transition metals (Ti, Mn, Co, Cu and Zn) may also show an influence of the pigment [13]. Also, the color in the rocks changes when heated at temperatures above 250–300 °C, which correspond to the dehydration of iron compounds. Pale brown colored rock change to reddish brown upon heating, which may not be apparent until the stones haves reached temperatures above 400 °C when goethite transforms to hematite [4,14,15].

Several investigations on the weathering mechanisms and degradation kinetics of Yucatan limestones have been reported [16,17], but little is known about the effect of thermal degradation on their mechanical properties. In this contribution, four types of limestone rocks, collected from the state of Yucatan (Southern Mexico), were investigated to elucidate correlations between rock compressive properties, mineral transformations and color change with thermal treatments at different temperatures as an attempt to simulate temperature changes similar to those observed in the "slash-and-burn" traditional systems in Yucatan.

2. Material and methods

2.1. Description of rock samples

The four types of rocks were selected from quarries of the Yucatan State, Mexico, which are used in the construction industry. These materials were selected considering their regional significance, abundance and frequency of usage as building and restoration materials [18]. The rocks were named "XCA", "CH", "LB", and "LR" after their Spanish acronyms. The sample XCA is a limestone with shades ranging from white to beige, inlaid with shells and fossils of snails with high porosity. CH is a limestone with different pale beige shades and high porosity. LB is a white compact limestone with low porosity, whereas the sample LR is a red compact limestone with low porosity.

The physical properties of the four limestone samples such as bulk density, water absorption, water content and effective porosity, were determined by water immersion based on mass difference and according to the ASTM standard D2216-98 [19] with three repetitions for each rock. For this purpose, a set of 12 cubic limestone samples were cut into coupons of 1 cm^3 obtained employing a low-speed diamond saw (Buehler Isomet).

2.2. Thermal treatment

Seven sets of rocks containing ten replicated limestone coupons were cut with a low-speed diamond saw (Buehler Isomet) for each temperature. The limestone coupons for thermal treatment comply with the dimensions set for (subsequent) compression testing with average dimensions of 21 mm × 10.5 mm × 10.5 mm, having a total of 280 prismatic coupons. The samples were polished with sandpaper in order to have a flat surface finish, and then cleaned using a sonicating bath. The samples were then washed with a 2:1 (v/v) mixture of water:acetone (J.T. Baker, 99.8%); afterwards they were left to dry at room temperature and set inside of an oven at 80 °C during 24 h.

Each set of samples were subjected to one of the six thermal treatments investigated with the targeted temperature fixed at 100, 200, 300, 400, 500 and 600 °C, using a heating rate of 3 °C/min to ensure thermal equilibrium of the limestone coupons. The targeted temperature was reached sequentially (step-wise) in steps of 100 °C maintained during 1 h, as depicted in Fig. 1. Additionally, a set of samples was kept at 25 °C to act as a blank. Once the targeted

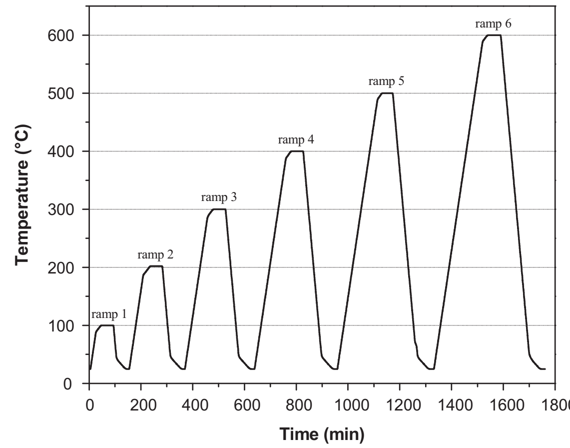

Fig. 1. Temperature treatment performed on the rocks before the compression tests. Heating was performed at a rate of 3 °C/min. The temperature steps (ramps) correspond to 100 °C, 200 °C, 300 °C, 400 °C, 500 °C and 600 °C.

temperature was reached, the samples were maintained during one hour at the corresponding temperature and the furnace was then cooled down slowly to room temperature in order to avoid sample cracking if suddenly are cooled. For example, for the test at 400 °C, the heat treatment followed the four initial ramps depicted in Fig. 1 requiring a total time of 16 h.

2.3. Sample characterization

The composition of specimens was analyzed using the powder X-ray diffraction technique (XRD Siemens D-5000) with a Bragg-Brentano geometry, a Cu-Kα radiation ($\lambda = 1.5418$ Å), scans with a step size of 0.02°, an integration time of 10 s and with a 2θ angular range of $5° \leq 2\theta \leq 50°$.

Thermogravimetric analysis (TG) and the derivative of the thermogram (DTG) were recorded in a Discovery TGA (TA Instruments). Powder samples (2 mg) were heated from 50 to 1000 °C applying a heating rate of 10 °C/min under an inert atmosphere (N_2).

Compression tests were conducted in a Shimadzu AGI-100 universal testing machine equipped with load cells of 5 kN and 100 kN and using a cross-head speed of 0.05 mm/min according to the ASTM standard D3148 [20]. The prismatic coupons for compression testing had a length of 21 mm and 10.5 mm × 10.5 mm cross-sectional area and ten replicates were tested for each thermal treatment.

To measure the reflectance spectra of the limestone materials as a function of the thermal treatment, the samples were illuminated with a deuterium-halogen light source (AvaLight DH-S-BAL) using an optical fiber; the light reflected was then collected using an integrating sphere (Labsphere USRS-99-010) and sent to a spectrometer (AvaSpec-2048) equipped with an optical fiber. The reflectance spectra were measured from 400 nm to 1000 nm. The color change was determined by applying the model of the *Commission Internationale de l'Eclaraige* (CIE), using as a standard illuminant D_{65} under an angle of 10° [21,22]. The color was described in terms of $L^*a^*b^*$ space color by CIE-LAB and CIELCH systems (CIE, 1976) [23], where the value of L^* represents lightness ($L^*=0$: black y $L^*=100$: white), and a^* and b^* chromaticity ($+a^*$=red and $-a^*$=green; $+b^*$=yellow and $-b^*$=blue) [24,25].

3. Results and discussion

3.1. Physical properties of the limestone rocks

The physical properties of the investigated limestone rocks such as bulk density and effective porosity were determined using