ANALES de Edificación

Received: 28-03-2019
Accepted: 12-04-2019

Anales de Edificación
Vol. 5, Nº 1, 66-71 (2019)
ISSN: 2444-1309
Doi: 10.20868/ade.2019.3915

Efectos de la humedad en piedras calizas para la construcción.
Effects of moisture on building limestones.

[1]Supriya Subramani, [2]F. Fernández, [2]A.J. Dos Santos, [3]M. del Río, [3]O. López

[1] SRM University, India (spriyasupriya@gmail.com); [2]Universidad Politécnica de Madrid (francisco.fernandezm@upm.es, aj.dossantos@upm.es, mercedes.delrio@upm.es, oscar.lopezz@upm.es)

Resumen— **El norte de España contiene una amplia variedad de piedras calizas destinadas a su uso en la construcción, con diversas características morfológicas y variedades de color. La mayoría de las calizas están compuestas de aragonita, aunque tanto calcita, como portlandita también se encuentran presentes en diferentes áreas de Europa. Su coloración más común es amarilla, blanca o marrón transparente. Las rocas en disolución ricas en calcio, favorece la deposición de caliza, produciéndose importantes cambios digeneticos. En esta ponencia se discutirán cómo la exposición a la humedad afecta a las calizas. Elementos tales como calcio, oxígeno, hidrógeno y carbono han sido identificados mediante análisis de difracción de rayos-x. Las calizas, en forma de carbonato de calcio e hidróxido de calcio, se someten a un tratamiento térmico y se analizan su rango de descomposición. Se calcula el porcentaje de pérdida de peso con respecto a la temperatura. Los resultados pueden ser utilizados por diseñadores de nuevos materiales y ayudar a desarrollar nuevos productos basados en calcita y con mejores propiedades técnicas.**

Palabras clave— Análisis térmico; propiedades térmicas; estudio de Rayos-X; piedras calizas naturales.

***Abstract*— North Spain contains a wide range of morphological and varieties of natural color limestones. Most of the limestones are composed of aragonite, but calcite and portlandite are also found in different areas of Europe. Their most common color is attractive transparent yellow, white and brown. Calcium rich dissolution rocks favors limestone deposition and produce important digenetic changes. In this paper we will discuss how digenesis modifies properties by exposing it in moisture. The elements such as calcium, oxygen, hydrogen and carbon were identified in power x-ray diffraction studies. The limestone known as calcium carbonate and calcium hydroxide is subjected to heat treatment and its decomposition range is analyzed. The percentage of weight loss with respect to temperature is calculated.**

Index Terms— Phase transformation; thermal analysis; thermal properties; X-ray techniques.

S. Subramani pertenece al Departamento de Física (Physics,Faculty of Engineering & Technology) de la SRM University - Ramapuram Campus: Ramapuram, Chennai, India.

F. Fernández y A.J. dos Santos pertenecen a la E.T.S. de Ingeniería y Diseño Industrial y M. del Rio y O. López a la E.T.S. de Edificación de la Universidad Politécnica de Madrid.

I. INTRODUCTION

Houses have been built with very few materials and techniques for hundreds of years until 18th century. The appearance of iron and reinforced concrete modifies the way of building and helps understanding modern architecture and cities (Crespo, 2009). The update of techniques and materials provided the window of using lighter and stronger compounds by introducing fibers in a polymer resin, whose characteristics will be more durable than concrete and steel materials (Marika and Herrmann, 2015).

According to the intergovernmental panel on climate change, it would be possible to save around 6,500 tons of CO_2 emissions until 2030 in the field of housing and construction worldwide by implementing efficient technologies (Onyeji and Günther, 1994).

Much of what was previously trusted to instinct or good luck is nowadays based on the application of constant discoveries in basic physics and chemistry. Designers of new material systems are using computer simulation to combine atoms (Maximilian et al., 2014) (Maya et al., 2014), calculate its molecular structure and deduce their physical and chemical properties. This helps to develop prototypes of actual models that are more likely to possess desirable properties, thus saving time and cost.

The above mentioned issue is a top priority for everybody involved in developing new building technologies and for those who participate in the process of quality management in building, particularly those related to testing or assessing in energy efficiency and sustainability studies in buildings or elaborate lifecycle studies of materials, building systems and buildings (e.g. Architects or Building Engineers).

II. STRUCTURE OF LIME STONES

Limestone naturally occurs in sedimentary rocks and in caves. The limestone known as “tufa” can be formed due to evaporation during the hot spring seasons in lake shore and other areas.

It is the naturally occurring mineral exists all over the world especially in central and north Spain and present in different form of crystal structures like (Fig. 1) calcite, aragonite and portlandite lime stones.

Fig. 2 explains about schematic diagram of atomic structure of calcite, aragonite and portlandite. In this large blue spheres, small black, pale and red spheres are Ca, C, H and O respectively.

The void space between the crystals determines the shape of the crystal, Since lime slaking is an integral part of treatment systems in water, waste water, air pollution, and process industries, its performance will influence the overall effectiveness of the process as well as operation costs (Potgieter et al., 2002).

The broadly used term "lime" denotes calcium-containing inorganic materials, which include carbonates; oxides and hydroxides of calcium, silicon, magnesium, aluminium, and iron predominate, such as limestone. By contrast, "quicklime" specifically applies to a single chemical compound. Quicklime is chemically known as calcium hydroxide, which is relatively inexpensive, and also important commodity chemical.

The production of calcium oxide from the limestone is one of the oldest chemical transformations produced by the man. Its use predates recorded history. The most ancient language like Latin the calcium oxide is known as “calx”, from which the name of the element calcium is taken. In old English language its name is “lïm”, which is the origin of the modern commercial name for calcium oxide, namely lime. The abundance of limestone in the earth's crust and the ease of its transformation to calcium oxide do not alone explain why the lime is one of the oldest products of chemistry. Lime has many properties that make it quite valuable.

The oldest use of lime exploits its capability to react with carbon dioxide to reproduce calcium carbonate. The mixture of sand, lime and water, which is used to construction the bricks, blocks, stones and bricks together. It can be used as stiff paste between the bricks. As shown in the Fig. 3 initially the stiff paste is laid between the bricks. It gradually hardens, cementing the bricks together. At room temperature, the reaction of lime with carbon dioxide is very slow. It is speeded when mixing

Fig. 1. Calcite, Aragonite (Calcium carbonate) and Portlandite (Calcium hydroxide).

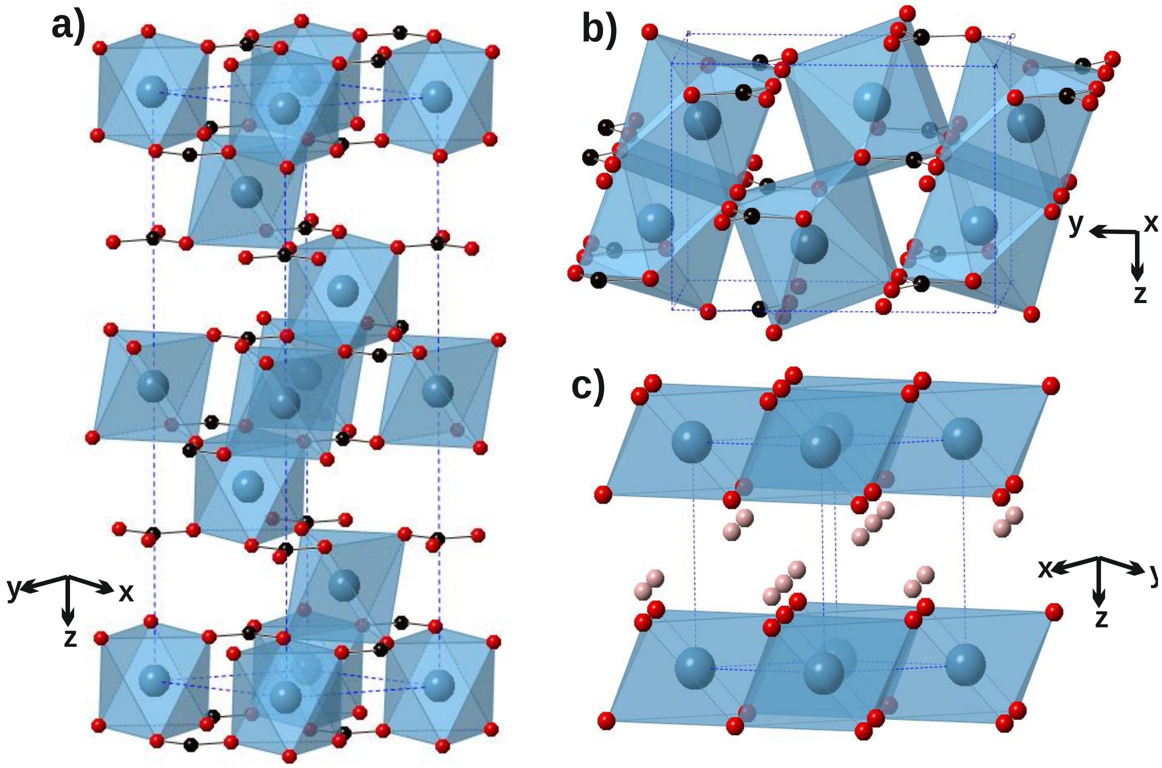


Fig. 2. Projections of a) calcite, b) aragonite and c) portlandite structures.

lime with water. When lime is mixed with water, it forms calcium hydroxide, called slaked lime (Zeman, 2008).

Even with the increased reaction speed, paste requires many years for complete reaction to occur. Other lime and ash-based products like lime plaster and portland cement can be used in the construction industries.

In mediterranean countries the mixture of slaking lime and $Ca(OH)_2$ with water is very typical use for painting outside and inside of buildings.

Fig. 3. Pasted bricks.

There are some useful characteristics:

1. Sanitary applications: Basic medium for non-ideal culture for bacteria.

2. The lime solution saturated during the penetration on building surface, the carbonation process occurs and forms a non-absorptive calcium carbonate, which slide over the material. In some deteriorated wall (Fig. 4) we can observe the multi slides produced in many applications over the years.

3.The produced calcium carbonate has white colour and reflect the visible spectra. This situation is ideal for hot seasons, which prevents from heat radiation of buildings (Fig. 5).

4. Linear thermal expansion coefficient of calcium carbonate is similar to the wall constructive materials and thermal stress deteriorations do not occur in contrast to organic painted surface damage.

III. REACTION OF LIME STONES IN MOISTURE

The calcium carbonate is heat treated at temperature about 600-700ºC and it produces calcium oxide from following equation (1):

(Limestone) $CaCO_3 + Q \rightarrow$ (Calcium Oxide) $CaO + CO_2\uparrow$ (1)

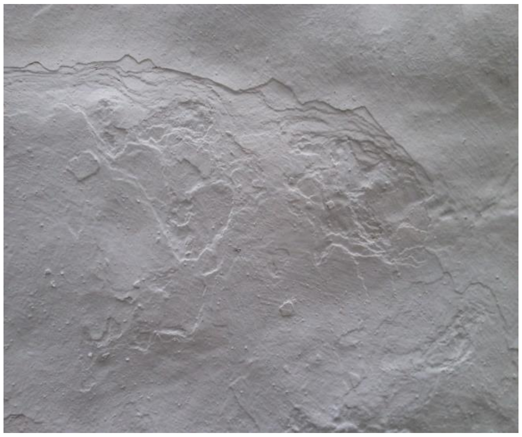


Fig. 4. Deteriorated wall with multiple slides.

Fig. 5. Calcium carbonate used in a typical Andalusian village as radiation prevention.

Calcium oxide (CaO), commonly known as quick lime or burnt lime and it is widely used as single or mixture form of chemical compound and also in building construction materials like cements. It is in white solid as pure form.

The hydration of CaO, commercially referred to as quick lime, is an exothermic process releasing a great quantity of heat. This hydration process when done with the right amount of water is called "dry hydration." In this case the hydrate material will be in the form of dry powder (Sébaïbi et al., 2006).

Quicklime produces heat energy by the formation of the hydrate, calcium hydroxide, by the following equation (2) and (3):

$$CaO\,(s) + H2O\,(l) \leftrightarrow Ca(OH)_2\,(l) \qquad (2)$$

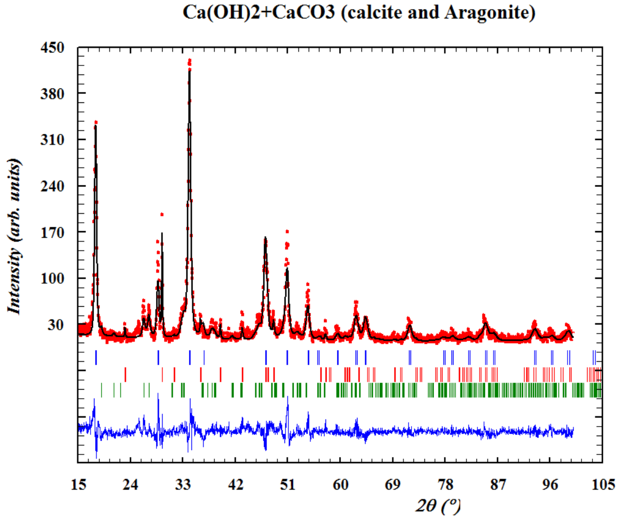


Fig. 6. Rietveld refinement data.

As it hydrates, an exothermic reaction occurs and the solid puffs up. The hydrate can be reconverted into quicklime by removing the water by heating it to redness by reversing the hydration reaction process. The energy liberated in this process and it can be used as the spot food warming in a self-heating process.

$$CaO(s) + H2O(l) \rightarrow Ca(OH)_2(s) \qquad (3)$$

Equation (4) explains about the reaction of calcium hydroxide with carbon di oxide is faster, producing a stiff paste that hardens more quickly.

$$Ca(OH)_2(s) + CO2(g) \rightarrow CaCO_3(s) + H_2O(l) \qquad (4)$$

However, CaO is unstable in the presence of moisture and react with the CO_2 and H_2O present in moisture and convert CaO to $CaCO_3$ and $Ca(OH)_2$, according equation (5) and (6)

$$CaO + H_2O\ (v) \rightarrow Ca(OH)_2 + Q \qquad (5)$$

$$CaO + CO_2\ \ (v) \rightarrow (\text{Limestone})\ CaCO_3 + Q \qquad (6)$$

Powder XRD data were collected using a Siemens D5000 diffractometer operating with Cu Kα radiation in the 2θ range of 15-100º with a step of 0.04º and counting time of 4 seconds. Thermal Analysis is made from Room Temperature to 1000ºC in nitrogen flow at heating rate of 20ºC/min.

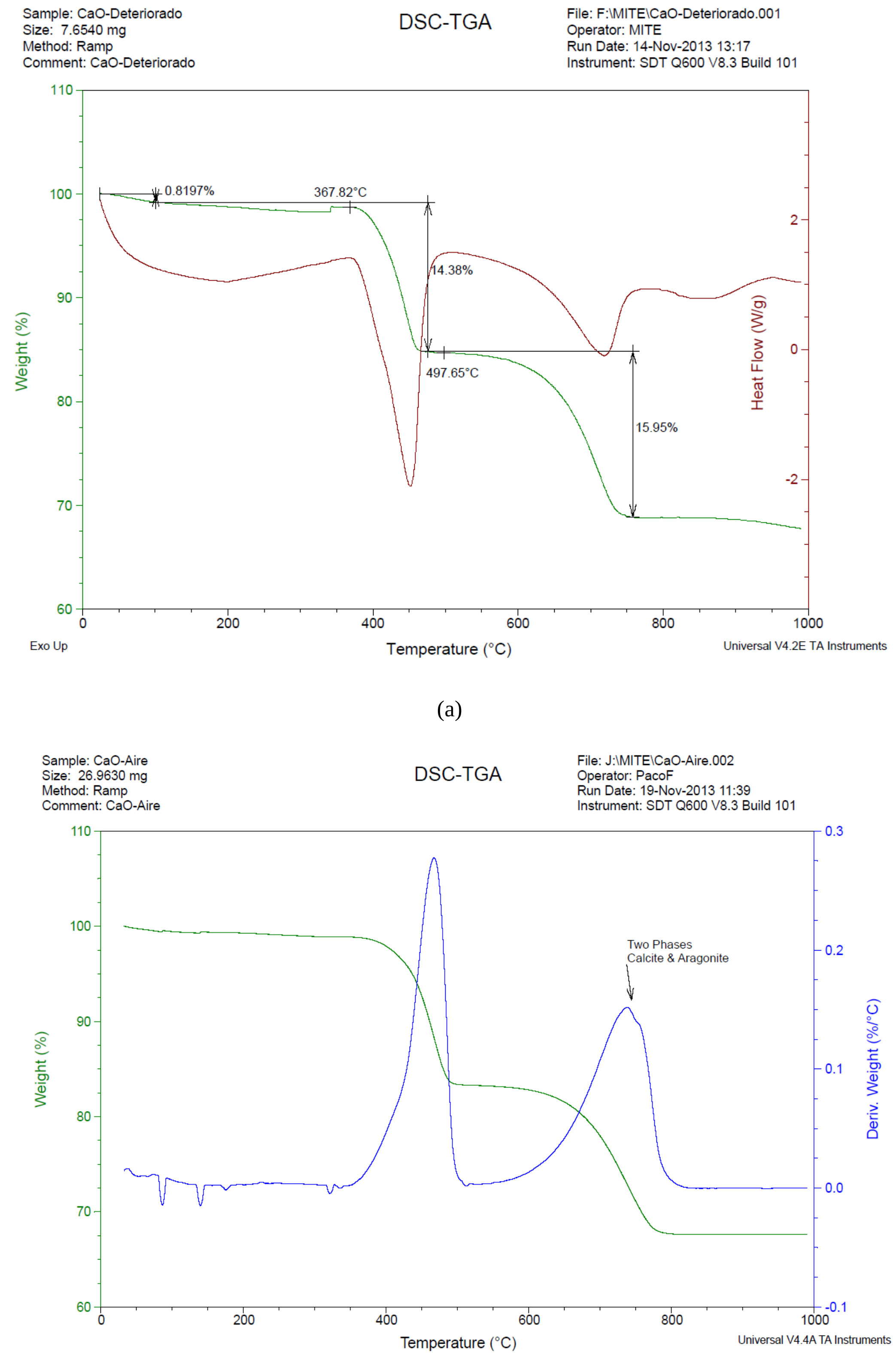
IV. RESULTS AND DISCUSSION

A. *Powder X-ray diffraction*

In order to explain what happens with the carbonate compounds, the powder X-ray diffraction data of the sample and the difference phases were observed during the analysis with EVA-program. In this program the possible elements Ca, O, H and C were chosen, and the qualitative analysis shows the presence of porlandite (calcium hydroxide), calcite and aragonite (two different phases of calcium carbonate).

In order to contrast the different data obtained from X-ray diffraction, FULLPROF program (Rodriguez, 1993) is used for quantitative analysis. The fitting of full profile refinement is present in Fig. 6.

Refinement data explains about the x-ray data of portlandite, calcite and aragonite with three phases. The phase 1, 2 and 3 represents the fractional % of 66.96 (1.10), 10.23 (0.47), 22.81 (0.97) of portlandite, calcite and aragonite respectively. From the figure the dotted lines represent the experimental data. Even line is calculated profile, lowest line shows the difference between experimental and calculated data. Vertical lines indicate the bragg position for different phases, first vertical line for portlandite, second vertical line for calcite and last



(a)

(b)

Fig. 7. (a) DSC-TGA of a sample of deteriorate CaO (exposed to moisture). (b) TGA and derivate weight loss curves of a sample of deteriorate CaO (exposed to moisture).

vertical for aragonite data.

B. *Thermal analysis*

The Differential scanning calorimetry and thermo gravimetric analysis (DSC-TGA) data (Fig. 7a & 7b) reveals the presence of two phases in the second decomposition, but it is not possible to separate and calculate the weight loss of the two compounds (calcite and aragonite-calcium carbonates).

V. CONCLUSION

The structure of calcite, aragonite and portlandite were analysed by powder x-ray diffraction. Its morphology was explained with schematic diagram. The thermal analysis data reveals the presence of two phases in calcite and aragonite samples. The phase transition, weight loss percentage was calculated. It is conceivable that insertion of water molecules could give rise to deterioration of natural building limestones.

REFERENCES

Crespo, S. (2009). Building materials for construction and civil works, Editorial University Club; San Vicente: Alicante, pp 1-10.

Marika, J., Herrmann, H. (2015). An orthotropic material model for steel fibre reinforced concrete based on the orientation distribution of fibres. Compos. Struct. 121, 324-336.

Maximilian, G., Ekaterina, E., Julian, S., Karsten, R., Heiko, B. (2014). Dissolution study of active pharmaceutical ingredients using molecular dynamics simulations with classical force fields. J. Cryst. Growth 405, 122-130.

Maya, D., Andrea, H., Luigi, B. (2014). Understanding Quality Requirements Engineering in Contract-Based Projects from the Perspective of Software Architects: An Exploratory Study. Rel. Sys. Qua. and Soft Archi. 1, 325-357.

Onyeji, C.S., Günther, F. (1994). An economic analysis of potential impacts of climate change in Egypt. Glob. Envir. change. 4(4), 281–299.

Potgieter, J.H., Potgieter, S., Moja, S.J., Mulaba-Bafubiandi, A. (2002). An empirical study of factors influencing lime slaking. Part I: production and storage conditions. Miner. Eng. 15, 201-203.

Rodriguez, J. (1993). Recent advances in magnetic structure determination by neutron powder diffraction + FullProf. Phys B: Condensed Matter 192, 55–56.

Sébaïbi, Y., Dheilly, Y.R.M., Beaudoin, B., Quéneudec, M. (2006). The effect of various slaked limes on the microstructure of a lime–cement–sand mortar. Cem. and Concr. Res. 36, 971-978.

Zeman F. (2008). Effect of steam hydration on performance of lime sorbent for CO_2 capture. Int. J. Greenhouse Gas Control 2, 203-209.