INFLUENȚA UNEI ATMOSFERE BOGATE ÎN CO_2 ASUPRA PROCESULUI DE ÎNTĂRIRE A ELEMENTELOR DE ZIDĂRIE PE BAZĂ DE CIMENT PORTLAND ŞI CENUŞĂ DE TERMOCENTRALĂ ACTIVATĂ

INFLUENCE OF CO_2 CURING IN ACTIVATED FLY ASH - PORTLAND CEMENT MASONRY UNITS

P. VALDEZ, G. FAJARDO, C. A. JUÁREZ*, A. DURÁN-HERRERA, J. A. DEL REAL

Universidad Autónoma de Nuevo León, UANL, FIC, Av. Universidad S/N, Ciudad Universitaria, San Nicolás de los Garza, Nuevo León, C.P. 66451, México.

Mixtures were designed to produce hollow masonry units (blocks) conform to Mexican specification; these blocks were subjected to a 60°C temperature and 90% relative humidity steam curing in an atmosphere of 20% CO_2 concentration. Thermo-gravimetric methods were used to evaluate the water vapor effect and carbonation in replicate pastes of the concrete blocks to determine portlandite, carbonates and CO_2 concentration in the block. Results illustrate that the application of CO_2 curing in activated fly ash-Portland cement masonry units can lead to 30% savings in cement consumption and to an average CO_2 fixation of 7% without modification of the compressive strength.

Keywords: *Concrete, Thermal analysis, Pozzolans, Lime, Portland cements.*

1. Introduction

As the foundation of the construction industry, cement production consumes significant amounts of natural resources and energy leading to greenhouse emissions composed by SO_x, NO_x and mainly CO_2 that contributes to important environmental issues related with global warming. In 2007, concrete industry consumed about 3.07 billion tons of cement, generating a large amount of CO_2 emissions as the main gas and energy consumption [1].

Feasible alternatives to reduce this problem consist in the use of industrial by-products that because their cementitious potential is refereed as complementary cementitious material when they are used together with Portland cement.

Fly ash (FA) is one of the major industrial by-products. In 2003, annual production in the United States was 68 million tons, of which only 34% was used in various applications among which concrete production stands out. In China, about 100 million tons FA are produced annually in coal-fired power plants, but only a quarter is used [2, 3].

Coal ash world production is estimated at about 600 million tons per year, of which fly ash is about 500 million tons, which represents 75 to 80% of the total worldwide production [4, 5]. Higher environmental benefits are anticipated by the use of fly ash in concrete production; diminution in the use of natural resources, contribute to improve sustainability in the concrete industry, improve durability of structures reduce energy consumption and greenhouse gas emissions. Fill lands will be reduced contributing to mitigate the risk of air pollution the health that this material can represent.

Threats many recent research works recommends the use of large amounts of fly ash and other industrial by products in the production of concrete masonry products such as concrete blocks, bricks and paving stones [6-9].

Previous research works have evaluated different fly ash activators in binary systems as fly ash-$Ca(OH)_2$, fly ash-cement and fly ash-lime-gypsum [10-14]. In combination with calcium hydroxide, fly ash can reduce the cement content in a Portland cement based system.

After hardening, the interaction of lime mortars with the environment will lead to carbonation and to changes in microstructure and tortuosity of pore network. Carbonation will lead to improve hardening and to reduce porosity, this will occur when moisture diminish within an optimum range and facilitate the reaction between $Ca(OH)_2$ and environmental CO_2 to form $CaCO_3$. Carbonation is a slow process that proceeds from the outer part to the inner part of the mortar.

The reaction mechanism by carbonation in a cementitious system produced with Portland cement is based on [15]:

a) Dissolution of CO_2 in the pore solution that later will react with calcium hydroxide.

b) Reaction of carbonic acid with silicates and aluminates.

Based on the reaction products and the effect of carbonation on un-reinforced concrete, it is possible to improve: the dimensional stability of the elements, permeability, compressive strength, chemical stability, abrasion strength and leaching [16, 17].

It has been shown [18-20] that curing of concrete un-reinforced masonry units in a CO_2-rich

* Autor corespondent/Corresponding author,
E-mail: cesar.juarezal@uanl.edu.mx

environment, is a feasible option to improve sustainability in masonry unit production. Due to the aforementioned reactions, carbonation is an advantageous option to sequestrate CO_2 within the cementitious matrix, and contribute to mitigate greenhouse emissions and associated global warming, This research was aimed to evaluate the effect of CO_2 curing in the physical and mechanical properties of concrete blocks manufactured with fly ash-Portland cement based binary systems or with fly ash-lime-Portland cement ternary systems under steam curing and accelerated carbonation.

2. Experimental methods

To evaluate the effect of CO_2 as a complementary curing technology in a controlled humid environment to improve concrete properties, prismatic hollow block-masonry units were produced with dimensions that meets the NMX C 404 Mexican specification [21], as illustrated in Figure 1.

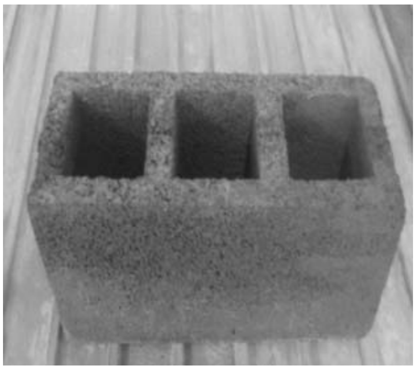

Fig. 1 - Concrete block (masonry unit) used to evaluate the properties targeted in this research.

2.1. Materials

Chemical composition of cementitious materials was determined by X-ray fluorescence spectroscopy and atomic absorption spectroscopy, according to ASTM-C-114 and ASTM-C-1084 [22, 23]. Physical properties and chemical composition of cementitious materials are presented in Tables 1 and 2.

Particle size distribution of cementitious materials was determined through a laser particle size analyzer Microtrac S 3500. The mineralogical compositions were determined by X ray diffraction. Fineness was determined according to ASTM-C-430 [24].

Table 2

Chemical composition of cementitious materials, % mass.

Composition	**PC**	**FA**	**L**
Silicon Dioxide (SiO_2)	21.2	72.7	0.8
Calcium Oxide (CaO)	62.9	1.4	98.1
Aluminum Oxide (Al_2O_3)	3.4	19.6	0.3
Ferric Oxide (Fe_2O_3)	1.8	2.2	0.1
Magnesium Oxide (MgO)	2.5	0.6	0.7
Potassium Oxide (K_2O)	0.7	0.6	0
Titanium Dioxide (TiO_2)	0	1.0	0
Sodium Oxide (Na_2O)	0.5	0.1	0
Loss on ignition to 900 °C	2.0	1.7	0
Sulfur trioxide (SO_3)	5.0	$<$ 0.1	0
Total	100	100	100
Equivalent Na_2O	0.9	0.5	----
SiO_2 + Al_2O_3 + Fe_2O_3	26.4	94.5	1.2

2.1.1. Ordinary Portland cement 40 (PC)

Ordinary Portland cement with an average particle size of 16 µm that meets the requirements for a type I cement according to ASTM-C-150 [25] specifications was used.

2.1.2. Fly ash (FA)

A fly ash that besides not meeting the fines requirements can be classified as class F according to ASTM-C-618 [26] was used. In order to control the uniformity of the particle size distribution, to reduce unburned coal content, to improve the strength activity index and to obtain the fraction that meets the requirements of ASTM-C-618, this fly ash was passed through the #200 sieve (75 µm). In Table 1 it can be observed that after the sieving process the obtained fraction of fly ash resulted with an average particle size of 31 µm, equivalent to a reduction of 60 % regarding the average particle diameter of the original fly ash.

2.1.3. Lime (L)

A construction lime (calcium hydroxide) commercially available in the northeast of Mexico that meets the requirements of the standard Mexican specification NMX-C-003 [27], and that has a greater fineness than the other cementitious materials considered in this project was used.

2.1.4. Aggregate

A 5 mm maximum size typical limestone sand locally used in the manufacture of masonry

Table 1

Physical properties of cementitious materials

Cementitious	Density g/cm^3	Average Particles Size µm	Fineness % Passing 325 (45µm)
Ordinary Portland Cement, PC	3.08	15.6	97.2
Fly Ash, FA	2.06	74.0	49.5
Fly Ash Screening, FAS	2.14	31.1	79.4
Lime*, L	2.25	9.3	98.5

*Calcium Hydroxide used in construction, it have a 90% of purity, according to manufacturer.

units was used with the following physical properties; density of 2.63 g/cm^3, absorption of 1.83% and a dry loose unit weight of 1,570 Kg/m^3.

2.1.5. Admixture

To facilitate the demoulding process of units, as well as to provide and maintain the appropriate consistency a plasticizer admixture was used, in a dosage of 124 mL/100 kg of cement.

2.1.6. Specimens Curing

After demoulding, to accelerate the hydration reaction, blocks were steam cured for 24 hours within an environmental chamber with controlled conditions of relative humidity (RH> 90%) and temperature (60°C). Then, units were subjected to a high CO_2 concentration exposure, under the following conditions: 20% of CO_2 concentration, exposure times of 24 and 48 hours, RH of 60 to 70 % and a temperature of 25 ± 2°C. Thereafter, blocks units were tested to determine water absorption and compressive strength.

2.2. Proportioning of mixtures, specimens manufacturing and evaluation methods

The final proportions of the concrete mixtures used in the manufacture of concrete blocks are presented in Tables 3, 4 and 5. Binary and ternary cementitious systems were produced by partial substitutions of fly ash and lime. Concrete blocks with dimensions of 400 x 200 x 150 mm were produced using a laboratory vibro-compression block making machine.

Once manufactured, specimens were cured for 24 hours in an environmental chamber, and afterwards dried at 110°C. Then, units were measured and subjected to the CO_2 curing process.

For each mixture, compressive strength was evaluated by triplicate according to the standard test method NMX-C-036 [28]. Water absorption of concrete blocks was obtained by duplicate according NMX-C-037 [29].

Table 3

Proportioning of mixtures reference and binary system cement – lime

Cementitious Substitution % weight of cementitious material	Cement kg/m^3	Lime kg/m^3	Water kg/m^3	Sand kg/m^3	Admixture kg/m^3
100 PC	167.0	0	100.0	2000.2	0.2
95PC + 5L	158.7	8.4	100.0	1997.6	0.2
90PC + 10L	150.3	16.7	100.0	1995.0	0.2
85PC + 15L	142.0	25.1	100.0	1992.3	0.2

Table 4

Proportioning of mixtures reference and ternary system cement – lime – fly ash unscreening

Cementitious Substitution % weight of cementitious material	Cement kg/m^3	Lime kg/m^3	Fly Ash kg/m^3	Water kg/m^3	Sand kg/m^3	Admixture kg/m^3
100 PC	167.0	0	0	100.0	2001.2	0.2
50PC + 5L + 45FA	83.5	8.4	75.2	100.0	1965.8	0.2
50PC + 10L + 40FA	83.5	16.7	66.8	100.0	1966.7	0.2
60PC + 5L + 35FA	100.2	8.4	58.5	100.0	1972.9	0.2
60PC + 10L + 30FA	100.2	16.7	50.1	100.0	1973.8	0.2
70PC + 5L + 25FA	116.9	8.4	41.8	100.0	1980.0	0.2
70PC + 10L + 20FA	116.9	16.7	33.4	100.0	1980.9	0.2
70PC + 15L + 15FA	116.9	25.1	25.1	100.0	1981.8	0.2

Table 5

Proportioning of mixtures reference and ternary system cement – lime – fly ash screening.

Cementitious Substitution % weight of cementitious material	Cement kg/m^3	Lime kg/m^3	Fly ash Screening kg/m^3	Water kg/m^3	Sand kg/m^3	Admixture kg/m^3
100 PC	167.0	0	0	100.0	2001.2	0.2
50PC + 5L + 45FAS	83.5	8.4	75.2	100.0	1969.4	0.2
50PC + 10L + 40FAS	83.5	16.7	66.8	100.0	1969.9	0.2
60PC + 5L + 35FAS	100.2	8.4	58.5	100.0	1975.7	0.2
60PC + 10L + 30FAS	100.2	16.7	50.1	100.0	1976.2	0.2
60PC + 15L + 25FAS	100.2	25.1	41.8	100.0	1976.7	0.2
70PC + 5L + 25FAS	116.9	8.4	41.8	100.0	1981.9	0.2
70PC + 10L + 20FAS	116.9	16.7	33.4	100.0	1982.5	0.2

In order to avoid the influence of the limestone aggregate in the quantification of portlandite, thermogravimetic analysis were performed using a SDT-Q600-TA equipment on pastes produced with the same water/binder proportion as in the mortar used to produce the masonry unit blocks. After mixing and before curing, each paste was isolated within a plastic bag were they hardened as specimens with average thickness of 3 mm. In preparation for the termogravimetric analysis, pastes were first subjected to water steam curing for 24 hours, and then subjected to a CO_2 curing for 24 hours. Stoichiometric analyses were performed in order to quantify the amount of CO_2 sequestrated by the paste in the concrete blocks.

3. Results and discussion

3.1. Compressive strength results

Compressive strength results of steam cured concrete blocks are reported in Figures 2, 3 and 4. All the mixtures produced with the binary system with lime, exceeds the strength required by NMX-C-404 [21] (5.9 MPa). During vibration and casting, it was observed that the 15 % of cement replacement by lime improves workability as expected in mixtures with these cementitious systems [30].

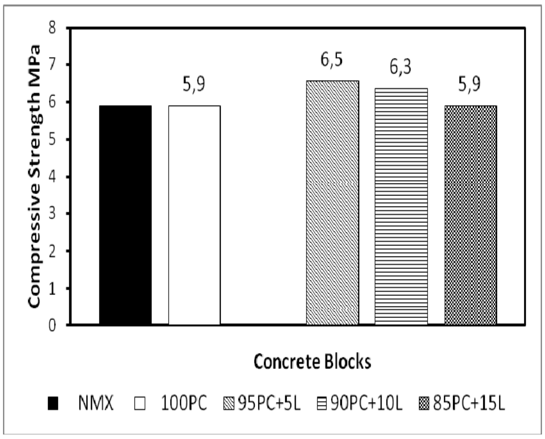

Fig. 2 - Compression strength of concrete blocks cured with steam for specimens reference and binary system PC – L.

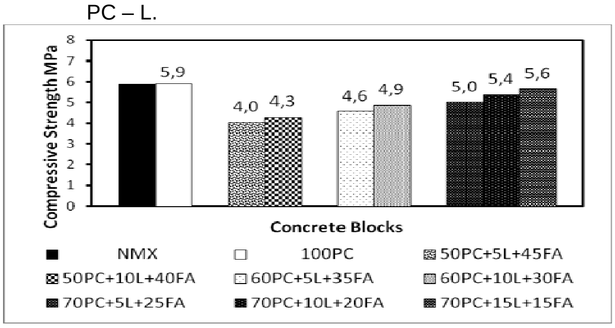

Fig. 3 - Compression strength of concrete blocks cured with steam for specimens reference and ternary system PC – L – FA.

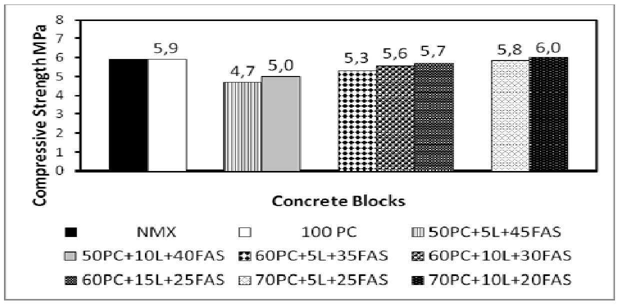

Fig. 4 - Compression strength of concrete blocks cured with steam for specimens reference and ternary system PC – L – FAS.

The compressive strength results for mixtures with ternary blends are shown in Figures 3 and 4. Mixtures reported in Figure 3 didn't satisfy the minimum compressive strength required by the specification. For mixtures with sieved fly ash this requirement was accomplished with a cement substitution of 30 %, labeled 70PC + 10 L + 20 FAS in Figure 4. Compared with non-sieved fly ash, as expected, it was evident that sieved fly ash improves pozolanic reactivity and consequently the strength development. Herrera et al [31], obtained approximately the same compressive strengths for similar cementitious systems and fly ash substitutions, for steam cured masonry units, with values higher than the strength required by the specification.

The compressive strength results of CO_2 cured concrete blocks are shown in Figures 5 and 6. The strength of blocks produced with binary blends resulted 14 % higher than the steam cured ones. This is attributed to the presence of higher amount of calcium carbonate within the pore network as a byproduct of carbonation. For ternary blends, the combined effect of lime and CO_2 curing contributed to obtain higher strengths and meet the minimum specified strength.

Water absorption was similar for all the mixtures, with no significant variations within batches. The range of values resulted between 6 and 8 % and lower to the maximum allowed value specified by the specification (12%).

3.2. Thermogravimetric analysis (TGA)

Thermogravimetric analyses were performed in cementitious pastes in a temperature range of 70 to 900°C to quantify the amount of calcium hydroxide and calcium carbonates. Figures 7 and 8 present the TGA/DTA curves for some of the pastes used in the manufacture of the masonry units. In this study, two segments of the cures were considered to evaluate the presence and amount of the compounds of interest, the first one is near to 450°C, where an abrupt mass loss occurs, which is attributable to calcium hydroxide dehydration. The second segment is located between 600°C and 750°C, where calcium

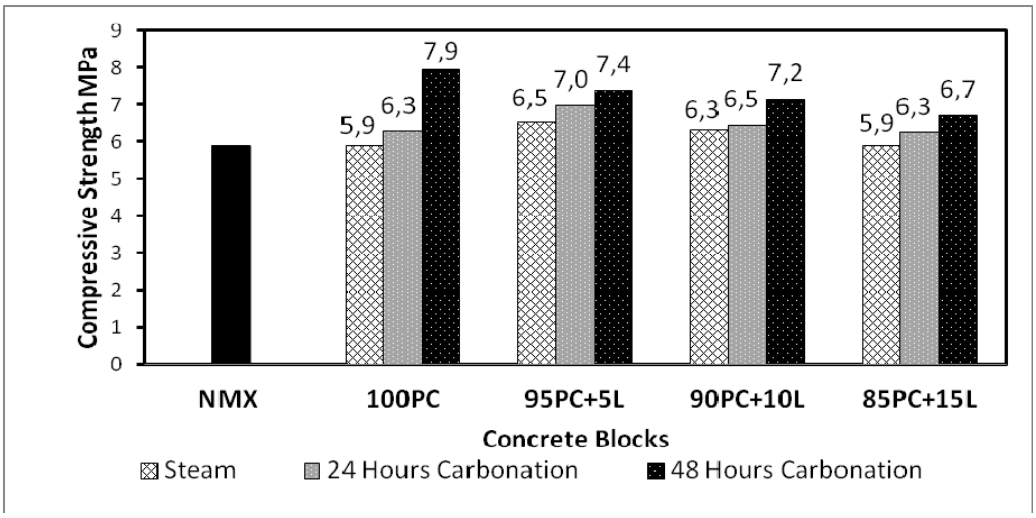

Fig. 5 - Compression strength of concrete blocks cured with CO_2 for specimens reference and binary system PC – L.

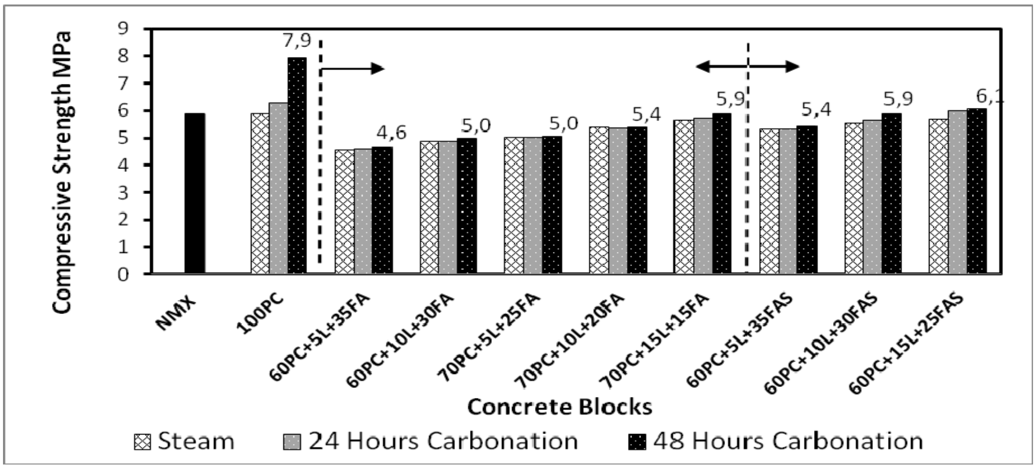

Fig. 6 - Compression strength of concrete blocks cured with CO_2 for specimens reference and ternary system PC – L – FA and PC – L - FAS.

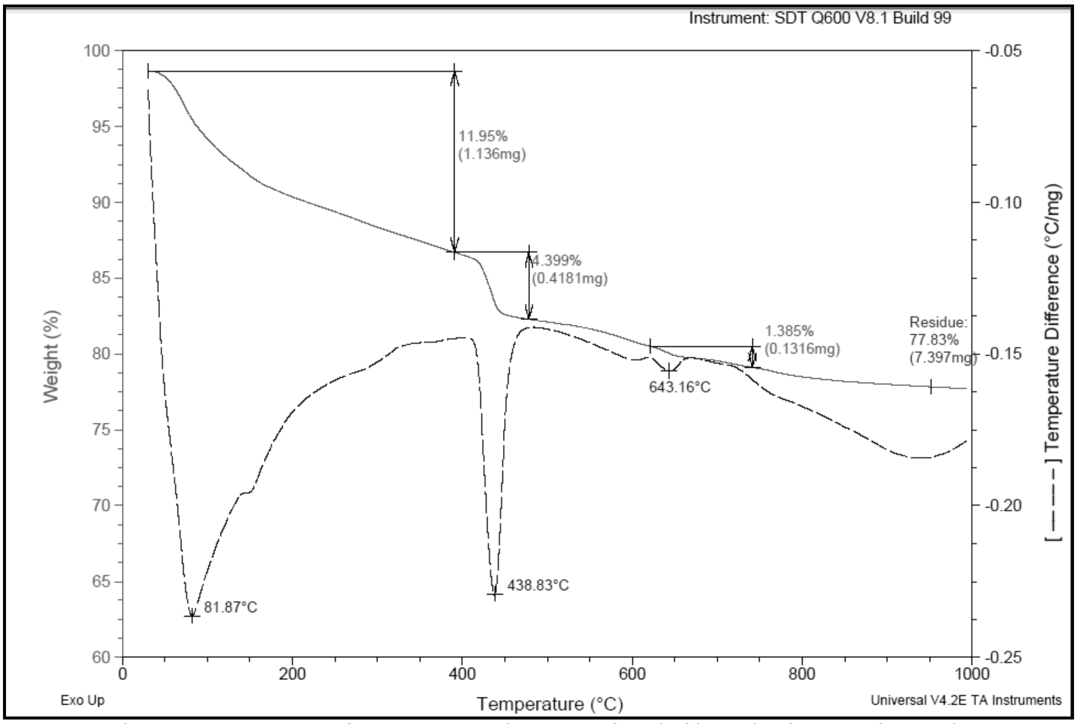

Fig. 7- TGA-DTA curves for a steam cured paste produced with Portland cement (100 CP).

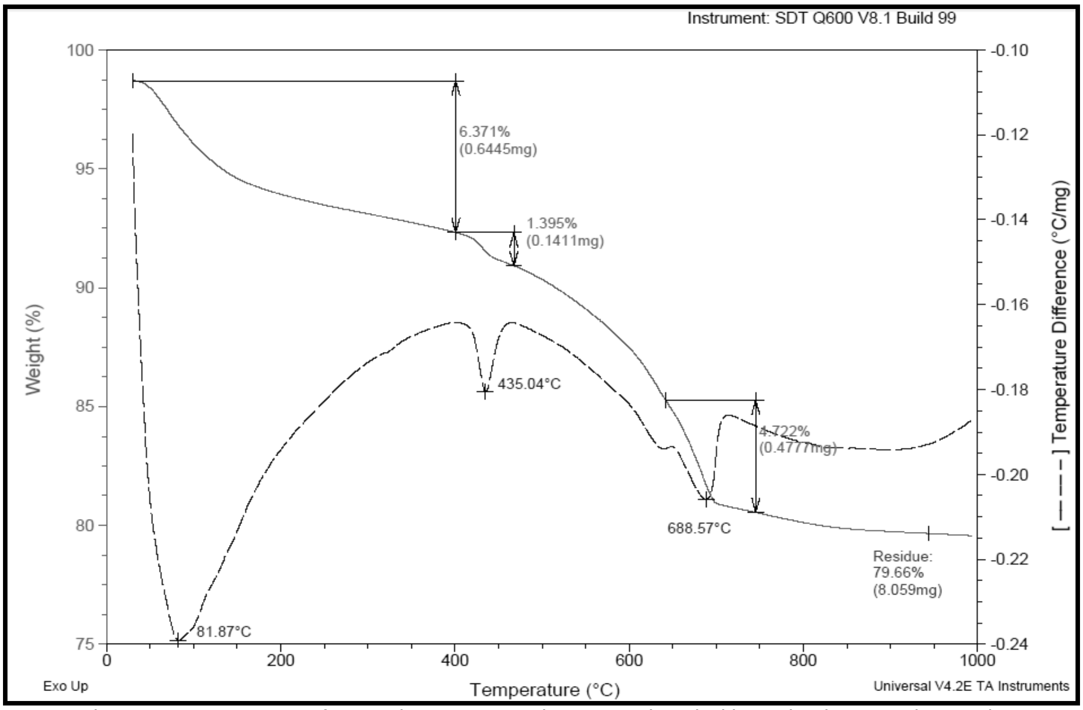

Fig. 8 - TGA-DTA curves for a 24 hour CO_2 cured paste produced with Portland cement (100 CP).

carbonates decomposition takes place. Compared with pastes steam cured, TGA/DTA curves for CO_2 cured pastes presented a higher mass loss attributed to the de-carbonation of calcium carbonate. Similar results were obtained for binary and ternary mixtures.

After curing, calcium hydroxide and calcium carbonate were determined for pastes cured for 24 and 48 hours to estimate the amount of CO_2 sequestrated or fixed in the cementitious paste.

Figure 9 present the $Ca(OH)_2$ and $CaCO_3$ for all the pastes considered in this study. In ternary mixtures were cement content was set in 60% of the total cementitious content, results illustrate that steam cured paste with fly ash consumes slightly more $Ca(OH)_2$ (1.6%) than those produced with FA. After CO_2 curing, $CaCO_3$ increases in the various mixtures to values between 6.9 to 20.6%. In binary pastes the average increase was about 14.5%, while the maximum reached value was 11.5 % for ternary mixture labeled as 60PC + 15L + 25FAS. In regards to reference mixture a substitution of 40 % of cement by fly ash and lime didn't originate a reduction in the masonry units' compressive strength. Fixation of CO_2 in CO_2 cured concrete blocks can be calculated by stoichiometry, results are presented in Table 6.

Table 6

Fixation of CO_2 on percentage for carbonated pastes by 24 hours.

Mixture	% CO_2 Fixed
100 PC	3.3
95 PC + 5 L	7.0
90 PC + 10 L	7.4
85 PC + 15 L	4.9
60 PC + 10 L + 30 FA	1.5
60 PC + 10 L + 30 FAS	3.7
60 PC + 15 L + 25 FAS	5.0

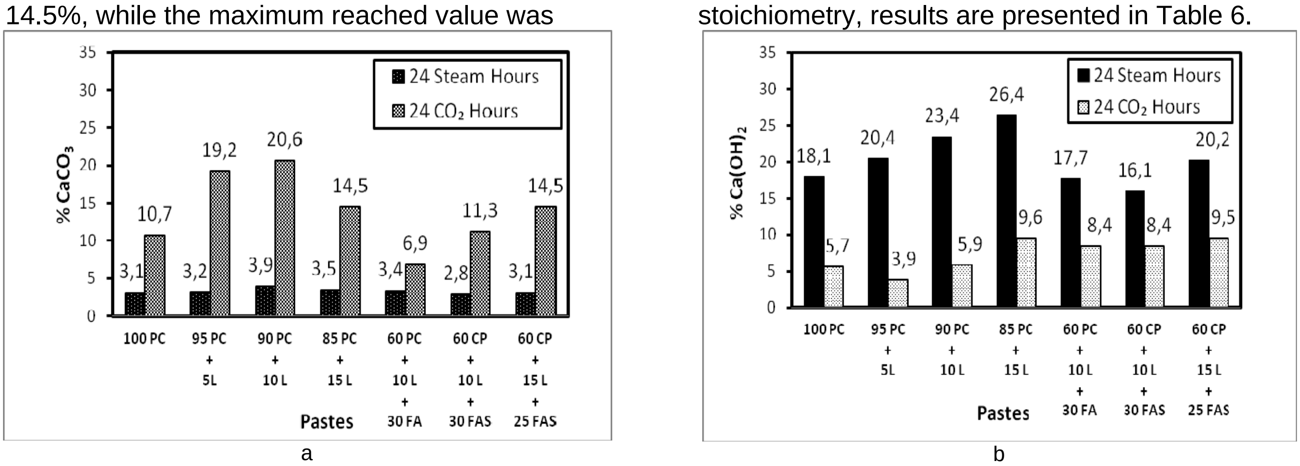

Fig. 9 - Percentage of calcium hydroxide (a) and calcium carbonate (b) in pastes cured with steam and CO_2 by 24 hours.

The results show a CO_2 fixation of 1.5 to 7.4%, in which binary mixtures have a higher fixation because they have greater quantity of $Ca(OH)_2$. Although, in ternary systems the fixation ranges from 1.5 to 5.0%.

4. Conclusions

Based on the results and comments, the following conclusions can be drawn:

- Concrete masonry blocks made with ternary blended cementitious mixtures and cement dosages of 40 % less than a typical mixtures meets the strength requirements of the Mexican standard specification. The incorporation of lime contributed to recover the compressive strength of the masonry units.
- CO_2 curing originated an increase in compressive strength for reference masonry units, as well as for masonry units made with binary and ternary cementitious systems.
- In terms of sustainability, in concrete masonry production, the combination of steam and CO_2 curing represents a technological added value and an effective way to sequestrate CO_2 without a detrimental effect on compressive strength.

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