Measurement of the speed of absorption of CO2 by Portland cement pastes and pure and additive mortars

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Abstract– We present here the results of experimental research on the speed of absorption of CO2 by Portland cement pastes and pure and additive mortars. The samples, introduced in a chamber, are exposed to a high concentration of CO2, simultaneously monitoring the temperature, relative humidity, pressure and concentration of CO2 present inside. The results show greater rapidity of carbonation both in cement pastes and in mortars when they are added with plasticizers, air incorporators or workability additives.

Keywords—accelerated carbonation, cement carbonation rate, CO2 capture, Carbonation resistance.

I. INTRODUCTION

The absorption characteristics of CO2 by cement pastes, mortars and concrete widely used in the construction industry have been studied extensively in recent years due to the large increase in the emission of CO2 into the atmosphere produced by the global cement industry [1]. The emission of CO2 when producing cement originates from the burning of fuel that feeds the kiln and the very process of Clinker formation in Portland cement [2]. The impact of CO2 produced by the cement industry can be mitigated by concrete recarbonation processes. Carbonation and recarbonation are identical processes that occur in concrete and involve the absorption of CO2.

Carbonation is a slow process associated with intact concrete structures. Recarbonation is an accelerated process that was initially observed in small pieces of concrete and ground concrete [3-4]. In this research we characterize the process of accelerated absorption of CO2 in samples consisting of Portland cement pastes and pure mortars and doped with additives of different composition.
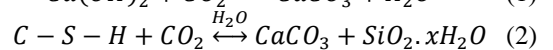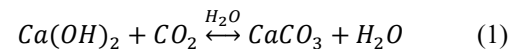
A. Cement paste carbonation:

Glasser et al. [5] have calculated the evolution of the different phases during the carbonation of a cement paste formed by C-S-H, portlandite and AFm monosulfoaluminate type. When starting carbonation at low partial pressures of CO2 monosulfoaluminate decomposes rapidly producing hemicarboaluminato. The liberated sulfate can react with a part of the aluminate and with the portlandite to give rise to the formation of ettringite secudaria AFt. As the CO2 concentration continues to increase, decomposition of the hemicarboaluminate and the formation of the monocarboaluminate take place. After these changes, the portlandite begins to carbonate until it disappears.

B. Concrete carbonation:

The high alkalinity of the concrete, which promotes the formation of a layer of passivating oxides on the steel, is mainly due to the portlandite formed during the hydration of the anhydrous compounds of the cement and to the sodium and potassium hydroxides present. These substances place the pH of the aqueous phase contained in the pores of the concrete in values between 12.6 and 14, at the most alkaline end of the pH scale. The decrease in alkalinity occurs mainly by reaction of the basic compounds of the aqueous phase of the concrete, sodium, potassium and calcium hydroxides, with the acidic components of the atmosphere, carbon dioxide (CO2) and sulfur (SO2), to form carbonates, sulfates and water. Since CO2 is found in a greater proportion in air than SO2, this process of decreasing alkalinity is generically called 'carbonation' [6]:

$$Ca(OH)_2 + CO_2 \overset{H_2O}{\longleftrightarrow} CaCO_3 + H_2O \qquad (1)$$

$$C - S - H + CO_2 \overset{H_2O}{\longleftrightarrow} CaCO_3 + SiO_2.xH_2O \quad (2)$$

The amount of CO2 required to lower the pH to almost neutral ranges, in which the reinforcements are no longer protected, varies depending on the alkaline reserve that the cement contributes to the concrete, which depends both on the type and amount of cement used.

Also, carbonation has a maximum for relative humidity around 50-60% [7-8]. The environmental conditions determine the moisture content in the concrete, which in turn determines the degree of water saturation in the pores, a fundamental parameter in the carbonation process. At low humidity, below 50%, the rate of carbonation is reduced by the need for a minimum presence of water for the reaction of the portlandite, while at very high humidity, the water of the pores hinders the diffusion of CO2 through from them. Temperature also influences the moisture content of concrete and the diffusion of CO2. In addition, the greater or lesser concentration of carbon dioxide in the exposure environment modifies the reaction rate and the evolution of water within the concrete.

II. EXPERIMENT

A. Schematic diagram of the carbonation measurement equipment.

A schematic diagram of the experimental arrangement for the observation of the rapidity of carbonation of samples consisting of cement pastes, mortars and concrete is shown in figure1The equipment allows simultaneous monitoring of the present concentration of CO2 in the chamber, its temperature, relative humidity and pressure inside while the sample is carbonated.
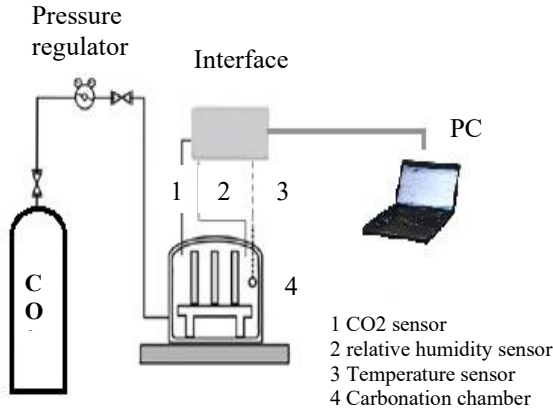
Fig. 1 The diagram shows a chamber with CO2 input at regulated pressure, whose interior is monitored in real time by sensors of CO2, relative humidity and temperature.

B. Carbonation chambers

Three carbonation chambers were implemented to observe the carbonation process of the samples, consisting of the absorption of about 80000 ppm of CO_2, in time intervals ranging from a few minutes to a few days.
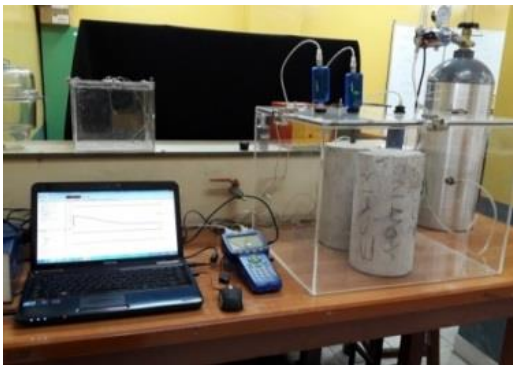

Figure 2. Carbonation chamber and sensors for monitoring the concentration of CO2, relative humidity, pressure and temperature inside.

C. Monitoring of temperature and relative humidity inside the carbonation chamber

Our observations of temperature and relative humidity within the chamber show small increases in temperature (<2 ° C) and considerable increase in relative humidity (> 10%) inside the chamber while carbonation occurs in both samples constituted by cement pastes and pure mortars or with additives. Typical curves of temperature and relative humidity versus time are shown in figures 3 and 4.
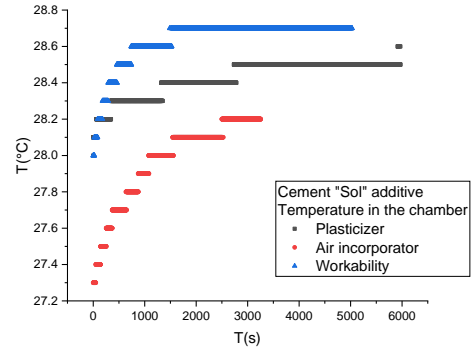

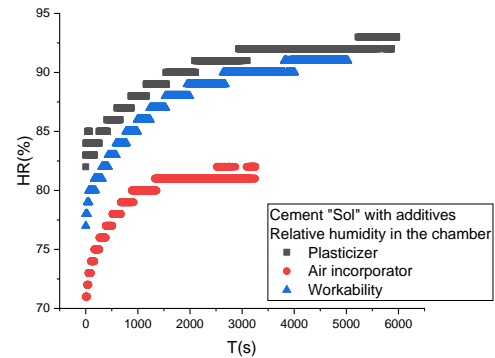Figure 3. Monitoring of the temperature inside the chamber during the carbonation of the samples.

Figure 4. Monitoring of relative humidity inside the chamber during the carbonation of the samples.

D. Dependence on the speed of accelerated carbonation with the exposed external area of the sample

We observe a strong dependence, on the rapidity of carbonation of the samples constituted by cement pastes, mortars and concrete, with the total external area exposed to the CO2 present in the chamber. Curves of concentration of CO2, present in the chamber (normalized in mass and initial concentration of CO2), versus time, are shown in Figure 5.
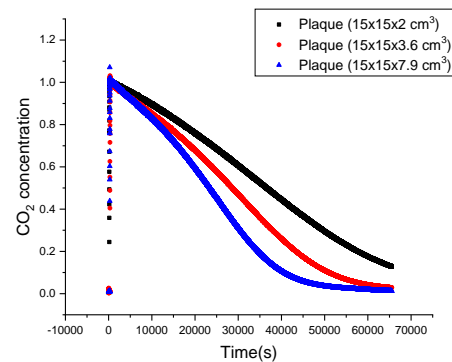

Figure 5. The curves show the dependence of the speed of carbonation of mortar to its external area exposed to the CO2 of the chamber.

E. Dependence on accelerated carbonation speed with cement composition.

We show here the results obtained by submitting accelerated carbonation Portland cement paste present in the domestic market. We observe that the pastes made with cements "Andino type V" and cement "Sol" are the ones that showed the least rapidity of carbonation.
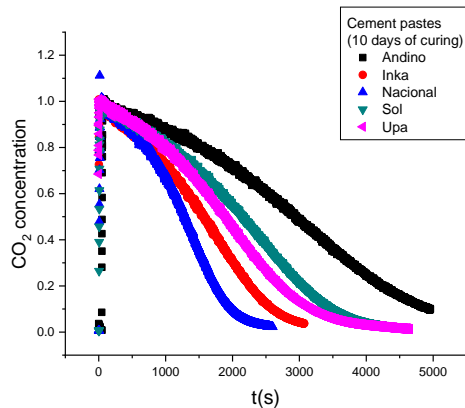

Figure 6. The curves show the rapidity of carbonation of pure pastes of commercial cements in the national market.

F. General XRD analysis for the identification of phase / composition of the cements.

To identify the composition of the cements whose carbonation curves are shown in Figure 6, we obtained their X-ray diffraction (XRD) spectra. The results are shown in figure 7.
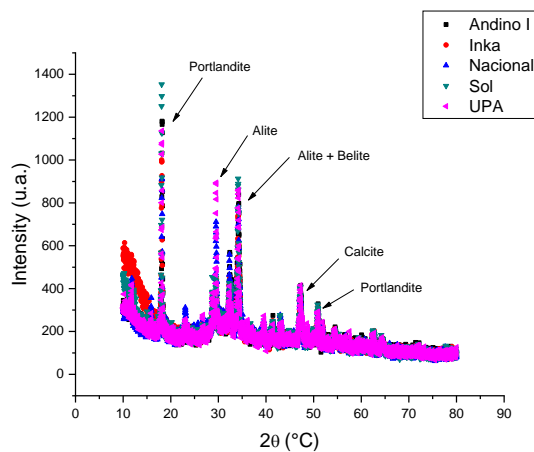

Figure 7. The DRX spectra of different types of carbonated cement pastes are shown.

All cements show similar curves of composition. The peaks corresponding to Portlandite, Alita, Belita, and calcite, typical components of Portland cement, can be identified [9-11].
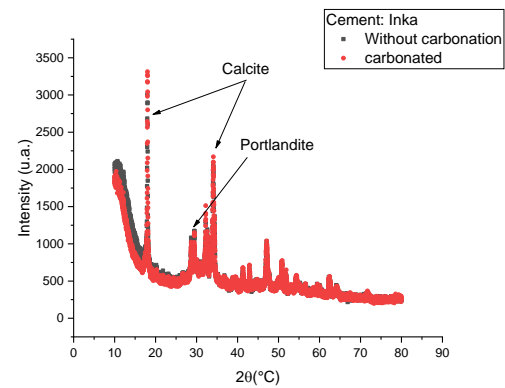

Figure 8. DRX spectra of Inka cement paste before and after its accelerated carbonation.

Figure 8 shows the DRX spectra of "Inka" cement pastes without carbonation (black curve) and carbonated (red curve). A slight increase in the concentration of calcite can be observed with a decrease in portlandite in the carbonated sample.

G. SEM Scanning Electron Microscopy

We obtained images of scanning electron microscopy (SEM), in order to obtain information on the changes in the microscopic structure of the cement pastes to be carbonated.
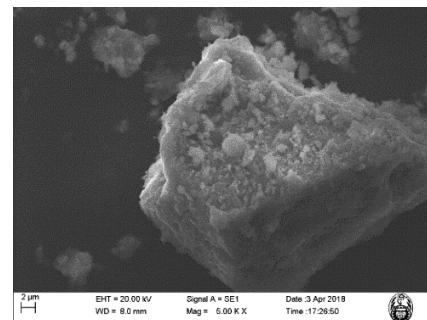

Figure 9. Portlandite crystal, surrounded by hydrated C3S granules. Scanning Electron Microscopy (SEM) UNI.
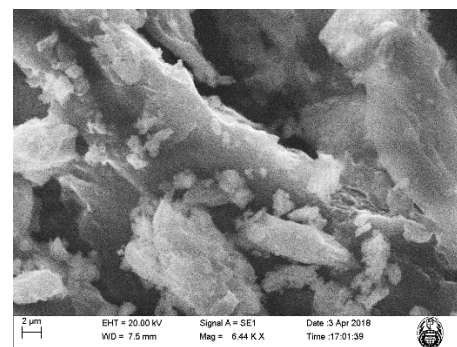

Figure 10. Carbonated "Inka" cement paste: Portlandite plates and CaCO3 nodules are observed. The image was obtained with 3500 increases.

Figures 9 and 10 show the structure of the Portlandite before and after carbonation. The increase in the presence of calcium carbonate nodules in the carbonated sample is observed.

H. Carbonation of cement "sol", pure and with additives

In order to observe the effect of the presence of additives on the speed of carbonation of the cement pastes, we doused the samples made with "Sol" cement:

Quantity of Cement: 500g

Amount of Water: 200g

Amount of Additive: 10g

Number of samples: 3 for each additive

Types of additives:

• Liquid waterproofing for concrete and mortar.

• Additive to improve the workability of concrete and water reducer to achieve concrete fluid, compact and durable.

• Plasticizer additive for mortar and concrete.

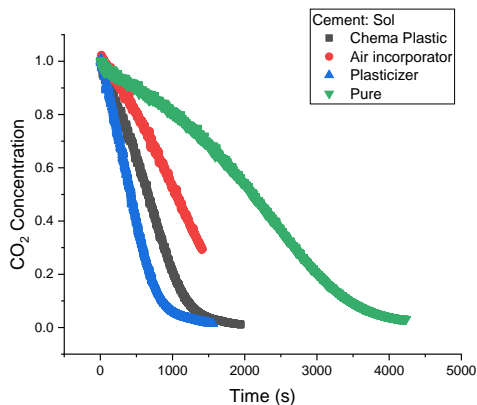The carbonation results of the additive cement pastes are shown in figure 11.

Figure 11. Accelerated carbonation curves of Sol cement paste doped with additives commonly used in our environment are shown.

The results indicate that the speed of carbonation increases when doping the cement paste with the different additives. The sample that presented the fastest carbonation was doped with the plasticizer additive.

Mortar carbonation

The mortars were prepared with "Sol" cement and modulus of fineness sand 3. A description of their compositions is shown in table 1.

The curing was performed by immersing the test pieces for 28 days in a solution obtained by mixing 3 g of lime per liter of water.

TABLE I
MORTARS COMPOSITION

	Without additive	A1	A2	A3	A4
Cement	260 gr	260 gr	260 gr	260 gr	260 gr
Sand	715 gr	715 gr	715 gr	715 gr	715 gr
Water	136 gr	144.6 gr	136 gr	130 gr	164.5 gr
Additive		5.2 gr	5.2 gr	5.2 gr	2.6 gr
Cement fluidity	109%	135%	119%	103.2 %	108.17
Fineness module	3	3	3	3	3.06

A1: Air-entraining additive
A2: Workability additive
A3: Additive plasticizer
A4: Carbon nanotubes additive

The results of accelerated carbonation of the mortars are shown in figure 12. Here again the increase in the speed of carbonation is observed when doping the mortar with the different additives.
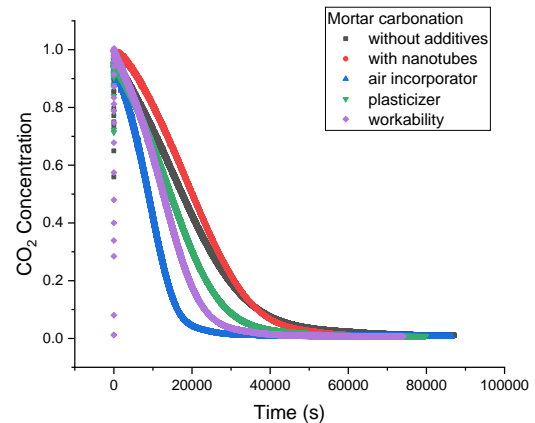

Figure 12. Accelerated carbonation curves of mortars prepared with "sol" cement, pure and additive.

The sample that presented the fastest carbonation speed was the doped with the air-entraining additive. The results obtained are consistent with results previously published by other authors [12-13].

Our results also show that, when doping the mortar with carbon nanotubes, the speed of carbonation decreases, which has also been reported in articles about the production of concrete called "intelligent", obtained by doping the concrete with carbon nanotubes [14- 15].

Conclusions

The experimental equipment implemented, allowed us to measure the speed of carbonation of cement pastes with different compositions.

The characterization of the accelerated carbonation process has been carried out. Measuring the influence of the exposed area of the sample, the influence of the relative humidity in the chamber, the influence of the different compositions of cements present in the national market, the influence of different additives commonly used in the construction industry.

Figures 3 and 4 show an increase in the temperature inside the carbonation chamber while the carbonation of the test pieces occurs.

Figure 5 shows a nonlinear dependency between the extent of the exposed external surface of the sample and the rate of carbonation. The carbonation rate increases with increasing the exposed surface of the sample.

Figure 6 shows differences in the carbonation speed of Portland-type cement pastes made by the different cement companies in Peru. XRD analysis (Figures 7, 8) showed small differences in the composition of the cements, mainly consisting of the percentages of Portlandite, Alite, Belite and Calcite present.

SEM microscopy was used to confirm the formation of the CaCO3 plaques due to the carbonation of the cement pastes (Figures 9,10).

The different types of Portland cement, and mortars prepared with this cement, were doped with type additives: air incorporators, plasticizers, and workability. A faster carbonation speed was observed in these samples, compared to the samples prepared with pure cement. However, when carbon nanotubes were used as a dopant, the lowest carbonation rates were obtained (Figures 11, 12).

We observed that the cement and mortar specimens prepared with carbon nanotubes presented the lowest carbonation speeds, which associated with their greater mechanical resistance and combined with their greater sensitivity to changes in their electrical resistivity via piezoelectric effects or variations in humidity or temperature of its bulk, make it an excellent candidate to be used in the manufacture of high-strength concrete and with appropriate characteristics to be used in monitoring structures (smart concrete).

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