INFLUENCE OF CARBON DIOXIDE AS A MIXTURE COMPONENT ON THE CEMENT HYDRATION

André Silva(1), Rita Nogueira(1), J. Alexandre Bogas(1) and Miguel Rodrigues(2)

(1) CERIS, ICIST, Instituto Superior Técnico, Universidade de Lisboa, Portugal

(2) Centro de Química Estrutural, CERENA, Instituto Superior Técnico, Universidade de Lisboa, Portugal

Abstract

Concrete is the most widely material used in the construction industry. However, it has a great environmental impact, mainly because of cement manufacture and the inherent CO_2 emissions into the atmosphere.

This research intends to contribute to the reduction of the environmental impact of the concrete industry through the uptake of CO_2 during the concrete production phase.

The few research works on this issue report contradictory results regarding the impact of CO_2 when added during the mixing phase. These results report an acceleration of the reactions [1], a reduction of the time setting [2] and either an increase or a decrease in the amount of hydration products, depending on the CO_2 amount [3, 1].

Thus, this research aims at understanding the impact of CO_2 amount on the hydration reactions of cement in order to enable its adoption as a component mixture.

To achieve this purpose, 4 cement pastes were produced with different amounts of CO_2. The pH of the mixture was measured to evaluate the impact of CO_2 on its alkalinity reduction. Compressive strength, XRD and SEM analysis were also performed to assess the influence on the hydration reactions and also on the degree of carbonation. Results suggest that CO_2 can increase the mechanical resistance at early ages if used in a little amount. However, the reduction in pH due to CO_2 appears to compromise this performance at longer ages.

Keywords: Carbonated water, Cement carbonation, Compressive strength, XRD, SEM

1. INTRODUCTION

The ease of application, versatility, good performance and availability of raw materials makes concrete the most widely used construction material, accounting for 70% of all construction materials. Concrete has, however, a high environmental impact due to the emission of carbon dioxide (CO_2) produced during the manufacturing of cement, namely in the calcination of limestone and combustion of fuels. Thus, it is estimated that this industry is responsible for at least 5% of the global CO_2 emission, annually [4, 5].

The reduction of the environmental impact associated with the production of cement has recently been the aim of scientific community and industry, with new strategies focused on capturing and incorporating the CO_2 in cement mixtures [6, 7]. However, these strategies have been mainly focused on the carbonation cure of freshly cast concrete, limiting the applicability of CO_2 usage in the concrete industry.

Although, CO_2 is naturally absorbed by concrete, the carbonation process is slow and only 8% to 28% of the reactive materials are estimated to be carbonated in the end of concrete life cycle [4, 5]. The mechanism of natural carbonation of cement is an extensively documented issue, and can be summarized by Eq. (1) and (2) that show how the two main components in life cycle of cement - portlandite ($Ca(OH)_2$) and calcium silicate hydrate (CSH, in cement chemistry notation) - react with CO_2 to form calcium carbonate ($CaCO_3$) and silica gel (SiO_2) [8, 1]:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{1}$$

$$CSH + 2CO_2 \rightarrow SiO_2 + 2CaCO_3 + H_2O \tag{2}$$

For the carbonation of freshly cast concrete, the mechanisms of early carbonation of cement can be summarized by Eq. (3) and (4), that show the carbonation of the dicalcium and tricalcium silicate (C_2S and C_3S, respectively, both according to the cement chemistry notation), producing a hybrid of calcium-silicate-hydrate and calcium carbonate [8, 1]:

$$C_3S + (3-x)CO_2 + yH_2O \rightarrow C_xSH_y + (3-x)CaCO_3 \tag{3}$$

$$C_2S + (2-x)CO_2 + yH_2O \rightarrow C_xSH_y + (2-x)CaCO_3 \tag{4}$$

Natural carbonation of mature concrete is an undesirable chemical reaction mainly because it decalcifies the concrete and reduces the pH value of the pore solution, leading to the depassivation of the reinforcement and consequently to steel corrosion. However, the carbonation at early ages can be beneficial, as it can be used as an accelerated curing technique [8, 1]. Different studies on carbonation techniques have been developed, mainly based on the curing of fresh concrete, reporting distinct results, namely, an acceleration of the reactions [1], a reduction of the time setting [2] and either an increase or a decrease in the amount of hydration products, depending on the CO_2 amount [3, 1].

The aim of this research is to study the influence of CO_2 on the hydration mechanisms of cement, focusing on the production phase of concrete instead of on the cure phase, strategy widely explored by other authors. For this purpose, CO_2 is provided to the mixing process as a mixture component, by being dissolved in the mixing water. Thus, the pre-carbonation of water provides the carbonate ions needed for the hydration and carbonation kinetics of cement, hence the CO_2 uptake is made during the concrete production instead of its aging.

To achieve this purpose, 4 cement pastes were produced with different amounts of CO_2. The reference sample (R-reference) and three other pastes made with increasing levels of dissolved CO_2 in the water (HC – high carbonated; MC – medium carbonated; and LC – low carbonated). The pH of the mixture was measured to evaluate the impact of CO_2 on its alkalinity reduction. Compressive strength, XRD analysis and scanning electron microscopy were also performed.

2. MATERIALS AND METHODS

2.1. Materials

The Portland Cement CEM I 42,5R used has a mineralogical composition of C_3S=56.7%, C_2S=16.6%, C_3A=10.0%, C_4AF=9.2% and a specific surface (Blaine) of 452 m^2/kg. The chemical composition of cement is CaO=62.76%, SiO_2=19.42%, Al_2O_3=26.00%,

Fe_2O_3=3.00%, Mg0=1.74%, K_20=0.53%, Na_2O=0.12%. The mixing water was provided by the main water supply. The CO_2 gas supply was provided by AirLiquide, at 99.995% purity.

2.2. Pre-carbonation of mixing water

The mixing water was pre-carbonated by pumping CO_2 into an airtight chamber containing water, following the setup illustrated in Figure 1. A container with 1300g of water was placed inside the chamber and the magnetic stirrer was set to give a rotation of 720rpm at a temperature of 25ºC. After closing the chamber, CO_2 was pumped for 20min at a constant flow, until a CO_2 concentration of 80% was reached.

Preliminary tests had determined that the saturation concentration of CO_2 in the water (1.68g/kg of water [9]) could be achieved by this procedure. The CO_2 concentration in the water was monitored by measuring the pH value of water (using a pH probe). The water quickly reached a pH value of ≈4.30, indicating the saturation concentration of CO_2 dissolved in the water previously mentioned [10].

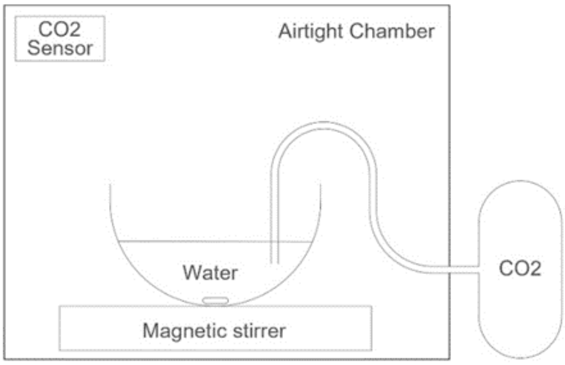

Figure 1: Schematic setup for the carbonation of water

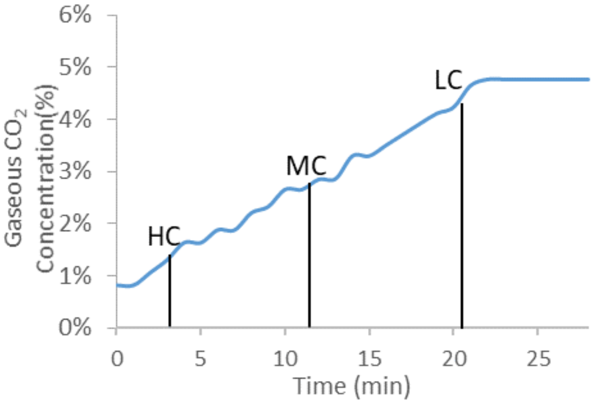

Figure 2: Concentration of gaseous CO2 inside the chamber

Then, the water thus obtained, was left waiting at room environment for defined sets of time, which led to different degrees of carbonation, through CO_2 release. Once the waiting time was over the water sample was mixed with the cement.

Preliminary tests were made to determine the CO_2 release rate, required to establish the diverse degrees of water carbonation and corresponding waiting time sets. Once the CO_2 concentration of 80% was achieved, the flow of gaseous CO_2 was shut and the door of the chamber was open for 1 min. This step allowed to the concentration of CO_2 in the environment inside the chamber to return to its initial concentration in the atmosphere. Then, the door was closed, and the growing of the CO_2 concentration was monitored (Figure 2). The CO_2 concentration took 21min to stabilize and increased at a constant rate. The aqueous CO_2 concentration over time was determined from gaseous CO_2 concentrations in the atmosphere, by Henry's law [11]. The diverse carbonated water samples are indicated in Figure 2 and in Table 1.

Table 1: Concentrations of the carbonated water samples

Sample	CO_2 concentration (mmol/L)
R	0.01
LC	5.09
MC	15.55
HC	26.01

2.3. Characterization of the cement pastes

Cement pastes were prepared with the diverse water samples, following the standard NP EN 196-1:2006. Specimens were cast in prismatic molds with 4x4x16cm^3, demoulded after 1 day and cured in a moist chamber until testing age. Tests were carried out at 1, 3, 7, 14 and 28 days of curing age.

Hydration and carbonation products formed in cement pastes samples were examined by X-Ray Diffraction (XRD) and Scanning Electron Images (SEM). For XRD and SEM a hydration stoppage method was applied at the different testing ages. The prismatic specimens were cut into smaller samples with 5x5x1cm^3 and put in 50ml of isopropanol for 15 min. Then, the sample was dried in an incubator at 40ºC for 10min and finally put inside a desiccator in vacuum until testing [12, 13].

For each sample, 4 compressive strength tests were performed at different curing ages, following the standard NP EN 196-1:2006.

The pH values of the pore solution were measured by grinding 30g of the sample into fine particles. Then, 30g of distilled water was added, corresponding to a ratio of 1:1, and this mixture was stirred. Finally, the value of the pore solution was measured using a pH probe [14].

3. RESULTS AND DISCUSSION

3.1. Compressive strength

Compressive strength results (Figure 3) show that the mechanical resistance tends to increase with the increasing of CO_2 concentration in the mixing water for the curing age of 3 days, but the opposite happens for the three higher ages (7 days, 14 days and 28 days).

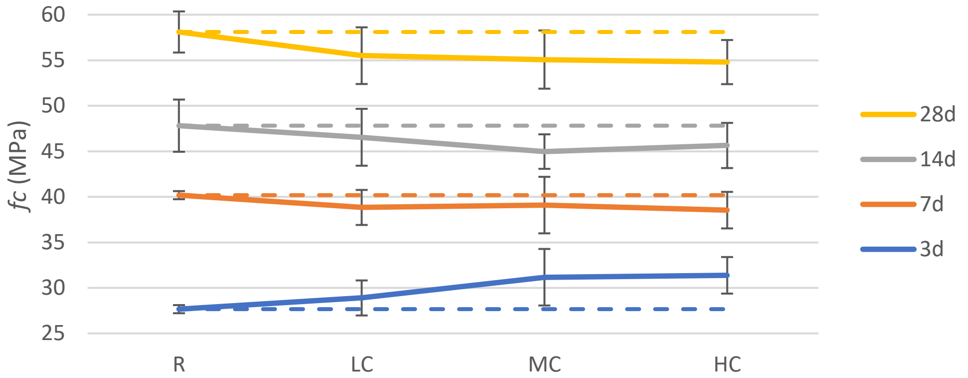

Figure 3: Compressive strength

These results suggest that CO_2 accelerates the cement setting at early ages; however, whichever are the reactions causing this acceleration, it seems that they penalize the development of the mechanical resistance immediately after.

The increase of the mechanical resistance is often explained by the higher amount of calcite returned by carbonation reactions, which tends fill pores, increasing the density of the mixtures [15, 16]. To investigate if this is the explanation for the compressive strength results, XRD analysis were performed to assess, namely, the amount of calcite in the different mixtures.

3.2. X-Ray diffraction (XRD)

Figure 4 shows the XRD results of reference sample (R), low CO_2 sample (LC), and high CO_2 sample (HC) in 4 different ages. XRD results were focused on the patterns of alite, belite, calcite (CC) and portlandite (CH) defined by the peaks 51.7º, 31.1º, 39.4º and 34.1º, respectively, as these peaks were selected as those values are free from peak overlapping [17].

The peak intensity of alite graph shows that, for 1 day, there is a higher consumption of alite for the sample HC and LC when compared with R. This result is also observed in the age of 3 days, but in a lower degree. The analysis of the following ages shows that there is a progressive consumption of alite, an observation also supported by the second smaller peak shown in the peak intensity of CH graph, which corresponds to alite instead of CH.

On the contrary, the peak intensity of belite graph shows a constant amount of belite in every tested age, suggesting that the compound was not consumed throughout the chemical reactions.

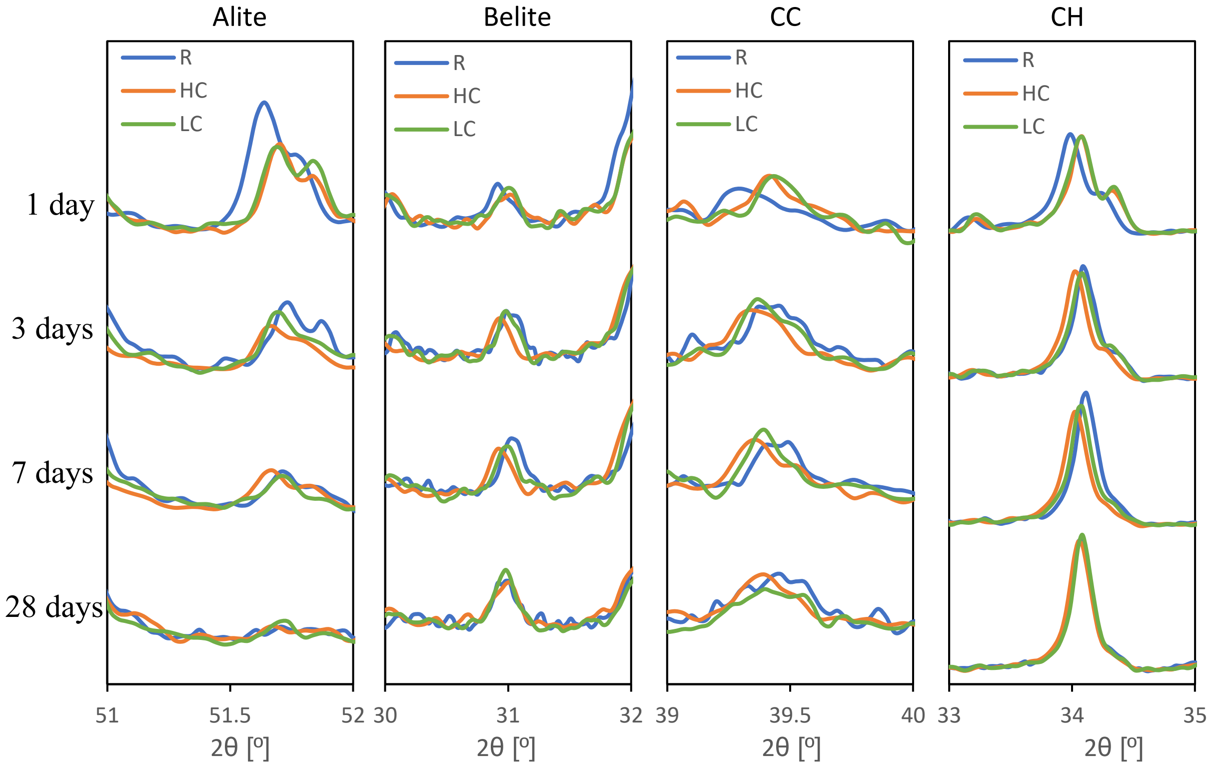

Figure 4: XRD patterns for alite, belite, CC and CH

The peak intensity of CC graph displays a slightly higher peak for HC and LC in comparison with the R sample, for 1 day. However, for the remaining ages, these peaks remain similar, showing that the formation of calcite crystals remains constant for the three samples. Following this result, also the CH shows, in the peak intensity of CH graph, a constant and similar quantity of CH in the three samples, even though the R sample exhibits slightly higher peak in every age, except for the 28 days.

These results suggest that CO_2 contributes to increase the dissolution rate of alite at early ages (1 and 3 days), which might be related with the higher compressive strength obtained in the CO_2-richer pastes with 3 days (Figure 3). In this situation, the dissolution of alite should have contributed to the formation of CC though the Eq. (3), followed by the consequent consumption of CH (Eq. 1). CSH is another product of this reaction and probably the component responsible for the increase in mechanical resistance observed in higher carbonated pastes at lower ages.

However, the mechanisms responsible for the inversion of this rising trend of the mechanical resistance for CO_2-richer pastes at later ages are not evident in the XRD results.

3.3. Scanning electron images (SEM)

SEM images were collected in HC and R pastes for the ages of 1 and 3 days, showed in Figure 5 and Figure 6.

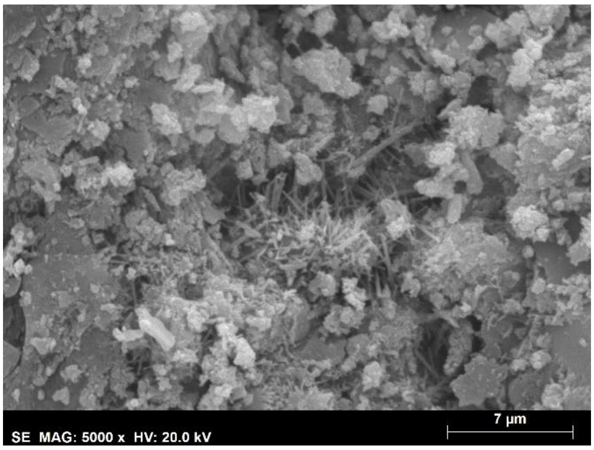

Figure 5:SEM image of a 1 day old HC sample

A macroanalysis of Figure 5 reveals a disperse set of reaction products across the surface of the cement grains with a considerable porosity between them. Figure 5 also shows the presence of needled structures, presumably ettringite, and products of cement chemical reactions of smaller sizes ($\approx 1\ \mu m$) on the surface of unreacted cement grains.

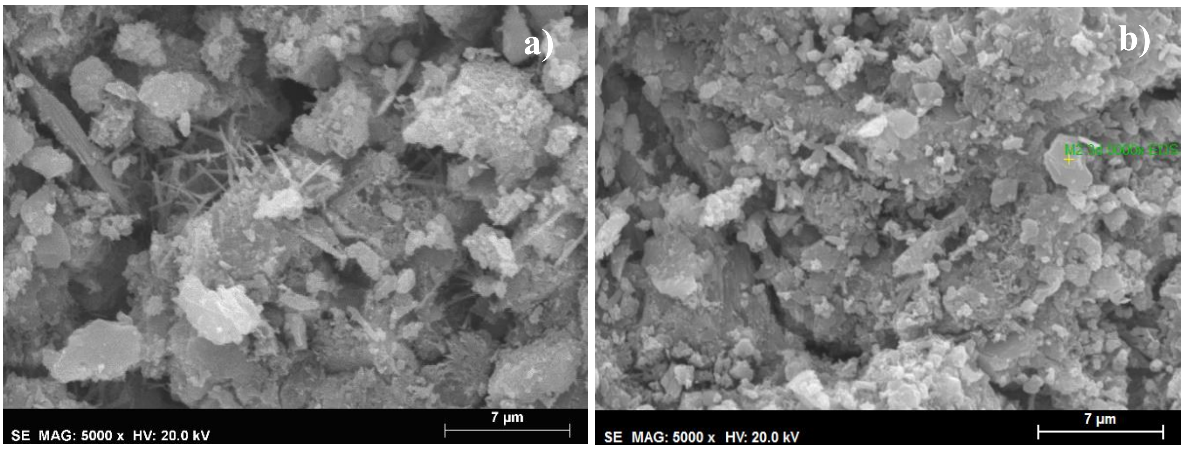

Figure 6: SEM images of a 3 days old R sample (a) and HC sample (b)

The analysis of Figure 6 shows that for the R sample (a) the products of cement reaction exhibit a bigger dimension ($\approx 2\ \mu m\ to\ 3\ \mu m$) than HC paste (b) of 3 days and 1 day (Figure 5). Needled structures were also found in the R sample (a). HC sample also shows the presence of needles, but in a lower amount, and the presence of calcite products identified through EDS (yellow cross in Figure 6b), illustrating the effect of carbonated water on the hydration reactions of cement. The lower presence of needles can be due to a quicker conversion of ettringite into calcium monosulfoaluminate [15]. Conversely the presence of calcite can be attributed to the carbonation of Ca^{2+} ions resulting from the hydration reactions [18, 19].

3.4. pH Measurement

Results from the pH measurement (Figure 7) suggest that for the curing age of 3 days the pH value is higher for LC both in relation to R-paste and CO_2-richer pastes (MC and HC).

However, the pH tends to increase with the curing age, stabilizing for a constant value of 12.7 observed in all the pastes at 28 days.

The pH results also suggest that, for the age of 28 days, each paste presents the same pH value, showing that cement paste carbonation in the early ages can produce specimens with pH values similar to uncarbonated concrete.

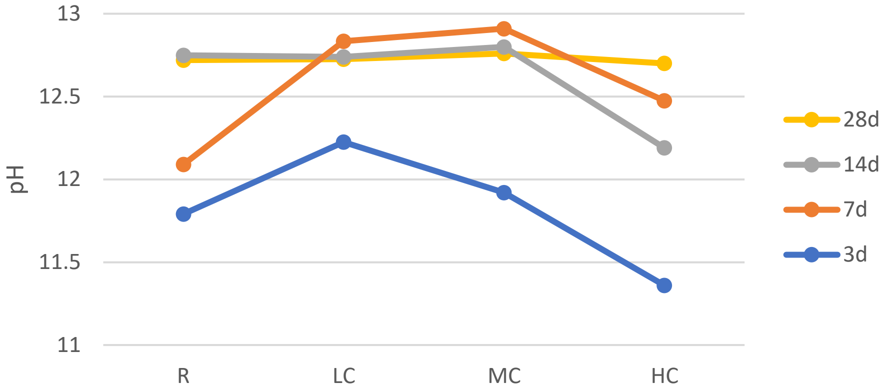

Figure 7: pH measurement results

These results suggest a combination of two opposite effects. On the one hand, the presence of CO_2 in the paste seems to cause an increase of the dissolution of alite at early ages, increasing the hydration and the mechanical resistance (Figure 3). At the same time, the formation of CH also increases, and the pH value rises (case of LC in Figure 7). On the other hand, for higher CO_2 concentrations, there is a consumption of CH (Eq. (5) and (6)) that is not made up by the higher CH release previously mentioned and the pH values drops (cases of MC e HC in Figure 7).

$$CO_{2(aq.)} + OH^- \leftrightarrows HCO^-_{3(aq)} \tag{5}$$

$$HCO^-_{3(aq)} + OH^-_{(aq)} \leftrightarrows H_2O + CO_3^{2-} \tag{6}$$

These considerations might explain the contradictory trends observed in the compressive strength results for early and later ages. A pH value higher than 11-12 is important to ensure the quality of the hydrated components of cement [20], since the silicate compounds loose reactivity for lower pH values [21].

Hence, it seems that CO_2 gives a positive effect at early ages because it contributes to the hydration of cement, but the effect is negative for later ages, because of the reduction in the pH values.

4. CONCLUSIONS

The impact of CO_2 in cement pastes in the mixing process studied in this article allowed to present the following conclusions:

- The presence of CO_2 in the initial stage of the process of hydration of cement has an effect on the initial compressive strength, leading to higher strengths. However, for the later ages this effected is reversed, leading to lower strengths for carbonated samples.
- The lower peak intensity of alite showed by the XRD results for the carbonated samples suggests that the presence of CO_2 in the mixture promotes an acceleration

of the hydration reactions of cement. Notice that this hydration is supposed to be associated to the production of CH and CSH.
- The SEM images showed the presence of hydration products with smaller dimensions for the carbonated samples and also the presence of calcite products, illustrating the effect of carbonate ions on the cement hydration kinetics.
- The pH results show that the presence of CO_2 increases the pH for early ages and for low CO_2 amounts, and the opposite happens for later ages and higher CO_2 concentrations.
- The results from the tests appear to justify the higher compressive strength for carbonated samples at early ages, due to the faster hydration reactions and the higher quantity of CC. For later ages, the lower compressive strength of the carbonated samples may be justified by the reduction in the pH value of the carbonated water.
- The pH value measurement result showed that even for carbonated samples, it can be achieved a pH value similar to uncarbonated concrete for the 28 days. This is an important result because it shows that problem regarding the depassivation of the reinforcement can be overcome when the carbonation is performed during the mixing process.

The results regarding the influence of CO_2 in the hydration reactions of cement presented in this paper set the base for further studies on this subject. Widening the applicability of the CO_2 usage in concrete production is a research area with a great potential as this paper and others demonstrate [19, 22, 23]. Further work should be focused on the application of the methodology in this paper to mortars and concrete, and the development of new ways to apply the carbonation technology to cementitious products.

5. ACKNOWLEDGEMENTS

This work was supported by the Polish National Agency for Academic Exchange under Grant No. PPI/APM/2019/1/00042/U/00001 and by the CERIS Research Centre, Instituto Superior Técnico, Universidade de Lisboa.

REFERENCES

[1] S. Monkman, M. MacDonald, P. Sandberg and R. Doug Hooton, “Properties and durability of concrete produced using CO2 as an accelerating admixture,” *Cement and Concrete Composites,* no. 74, pp. 218-224, 2016.

[2] F. C. Jorge, C. Pereira and J. M. Ferreira, “Wood-cement composites: a review,” *Holz Roh Werkst,* no. 62, pp. 370-377, 2004.

[3] J. Kwasny, P. Muhammed Basheer and M. Russell, “CO2 Sequestration in Cement-Based Materials During Mixing Process Using Carbonated Water and Gaseous CO2,” *4th International Conference on the Durability of Concrete Structures,* 2014.

[4] P. K. Metha, “Reducing the environmental impact of concrete: concrete can be durable and environmentally friendly,” *Concrete International,* vol. 10, pp. 61-66, 2001.

[5] C. Pade and M. Guimaraes, “The CO2 uptake of concrete in a 100 year perspective,” *Cem. Concr. Re,* vol. 37, pp. 1348-1356, 2007.

[6] L. Haselbach and Thomle J., “An alternative mechanism for accelerated carbon sequestration in concrete,” *Sustainable Cities and Society,* vol. 12, pp. 25-30, 2014.

[7] P. He, C. Shi, Z. Tu, C. Sun Poon and J. Zhang, “Effect of further water curing on compressive strength and microstructure of CO2-cured concrete,” *Cem. Concr. Compos.,* vol. 72, pp. 80-88, 2016.

[8] V. Rostami, Y. Shao, A. Boyd and Z. He, “Microstructure of cement paste subject to early carbonation curing,” *Cem. Concr. Res.,* vol. 42, pp. 186-193, 2012.

[9] J. A. Dean, Lange´s Handbook of Chemistry, 15º ed., University of Tennessee, Knoxville: McGraw-Hill, Inc., 1999.

[10] S. E. Manahan, Environmental Chemistry, 9º ed., Boca Raton: CRC Press, 2010.

[11] R. Sander, “Compilation of Henry's law constants (version 4.0) for water as solvent,” *Atmospheric Chemistry and Physics,* no. 15, pp. 4399-4981, 2015.

[12] J. Zhang and G. W. Scherer, “Comparison of methods for arresting hydration of cement,” *Cement and Concrete Research,* no. 41, pp. 1024-1036, 2011.

[13] K. Scrivener, R. Snellings and B. Lothenbach, A Pratical Guide to Microstructural Analysis of Cementitious Materials, CRC Press, 2016.

[14] A. Behnood, K. V. Tittelboom and N. D. Belie, “Methods for measuring pH in concrete: A review,” *Construction and Building Materials,* no. 105, pp. 176-188, 2016.

[15] X. Qian, J. Wang, Y. Fang and L. Wang, “Carbon dioxide as an admixture for better performance of OPC-based concrete,” *Journal of CO2 Utilization,* no. 25, pp. 31-38, 2018.

[16] E. Possana, W. Thomazc, G. Aleandric, E. Felixa and A. Santos, “CO2 uptake potential due to concrete carbonation: A case study.,” *Case Studies in Construction Materials,* vol. 6, pp. 147-161, 2017.

[17] J. Jang and H. Lee, “Microstructural densification and CO2 uptake promoted by the carbonation curing of belite-rich Portland cement,” *Cem. Concr. Res.,* vol. 82, pp. 50-57, 2016.

[18] N. Lippiatt and T.-C. Ling, “Rapid hydration mechanism of carbonic acid and cement,” *Journal of Building Engineering,* no. 31, p. 101357, 2020.

[19] D. Zhang, Z. Ghouleh and Y. Shao, “Review on carbonation curing of cement-based materials,” *Journal of CO2 Utilization,* vol. 21, pp. 119-131, 2017.

[20] W. K. W. Lee and J. S. J. v. Deventer, “The effect of ionic contaminants on the early-age properties alkali-activated fly ash-based cements,” *Cement and Concrete Research,* no. 32, pp. 577-584, 2002.

[21] F. Pacheco-Torgal, J. Castro-Gomes and S. Jalali, “Alkali-activated binders: A review Part 1. Historical background, terminology, reaction mechanisms and hydration products,” *Construction and Building Materials,* no. 22, pp. 1305-1314, 2008.

[22] M. F. Bertos, S. J. R. Simons, C. D. Hills and P. J. Carey, “A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO2,” *Journal of Hazardous Materials,* no. B112, pp. 193-205, 2004.

[23] J. Jang, G. Kim, H. Kim and H. Lee, “Review on recent advances in CO2 utilization and sequestration technologies in cement-based materials,” *Constr. Build. Mater.,* vol. 127, pp. 762-773, 2016.