EARLY-AGE CARBONATION OF CALCIUM SILICATE HYDRATE (C-S-H) AND ITS ABILITY FOR CO_2 SEQUESTRATION IN CONCRETE

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ABSTRACT: The research trend in the last years on early-age carbonation of calcium silicate hydrate, main component phase of Portland cement, in association with the process of permanent storage of CO_2 in carbonates, reducing its emissions in the atmosphere, was the objective of ongoing work. Using sodium bicarbonate ($NaHCO_3$) in the mixture of cementitious materials, partially replacing the cement (between 7-21 %), curing the fresh concrete was made in an early-age period. Very high value of compressive strength (43.1 MPa) was obtained very quickly being measured in the first stage of investigating the sample characteristics (after 8 hours), the reference sample reaching 30.8 MPa after 7 days and 43.3 MPa after 28 days.
KEYWORDS: calcium silicate hydrate, Portland cement, early-age, CO_2 sequestration, sodium bicarbonate, compressive strength.

1. INTRODUCTION

The actual conditions of environmentally friendly crisis in the world caused by tendency of the earth's atmosphere to overheat have strongly affected the cement industry and implicitly the construction sector. Excessively high emissions of carbon dioxide (CO_2) have led to radical measures at the global level regarding the prospects of cement manufacturing as the main feedstock for producing the building concrete. The main decision of the international institutions regarding the cement manufacture was the drastic reduction of its production, thus implying the need for new solutions of cementitious materials with pozzolanic properties from suitable recycled waste (coal fly ash, granulated blast furnace slag, rice husk ash, red mud, etc.) [1].

The remarkable invention of the French researcher Davidovits [2] offered the option of manufacturing geopolymers based on alumino-silicate materials in their natural state (metakaolin) or as industrial by-products (fly ash, blast furnace slag, etc.) [3].

Concerns of scientists in the last time have been concentrated on the sequestration of CO_2 in concrete as a result of early-age carbonation of calcium silicate hydrate (named C-S-H), the main binding component of the Portland cement [4]. Tri- and di-calcium silicate ($3CaO \cdot SiO_2$ or C_3S, and $2CaO \cdot SiO_2$ or C_2S) are the mentioned component phases of cement. By mixing with water (hydration), the cement phases (known also as alite and belite, respectively) representing about 75 % of the modern cement mass have special importance on its properties (setting time and strength) [5, 6].

According to the paper [4], carbonation reactions that take place during the cement hydration in the early stage significantly differ compared to those that occur in the late phase. The relatively destructive nature of carbonating the cured Portland cement leads to material contraction phenomena, which generate micro-cracks affecting its structural compactness. This type of forced carbonation of binder ultimately leads to creating calcium silicate hydrate phases as a gel. For higher amounts of gaseous CO_2, it continues to react with C-S-H, generating a mixture that includes $CaCO_3$ and SiO_2 gel. Intensifying the curing process due to the forced carbonation of the fresh concrete can significantly improve the mechanical and chemical resistance (to chloride), the resistance to freeze-thaw cycles as well as the reduction of the water absorption level. Tests performed by Loh et al. in 2021 [7], aiming at the hydration of cement in early stages, have found the generation of a transient phase of calcium hydroxide (noted further as CHt) before the start of setting.

This transition phase could be used to sequester CO_2 as a stable carbonate mineral. The pre-curing carbonation of cement, according to Stefaniuk et al. [4], does not affect the material structure and leads to the integration of CO_2 in maximum proportions of 15 % in the form of calcite and a composite phase including $CaCO_3$ and C-S-H. The composite phase contains several polymorphs of $CaCO_3$, which finally turn into calcite, considered in terms of

chemistry as the most stable form of $CaCO_3$. Microscopic examination of early stages of hydration revealed phase transformations caused by experimental substitutions of up to 20 % of $CaCO_3$ with sodium bicarbonate ($NaHCO_3$). Except for the formation of tri-calcium silicate ($3CaO \cdot SiO_2$), C-S-H, and calcium hydroxide, the presence of several $CaCO_3$ polymorphs and hydrates was discovered. Experimental results described in [4] showed that by advancing the carbonation during the pre-curing stage (fresh mixing stage), the mineralized calcium carbonates can constitute stable storage sites for CO_2 in the composite formed by $CaCO_3$ and C-S-H, ensuring a partial compensation (up to 15 %) by mineralizing the CO_2 emissions together with the made clinker and thus leading to obtaining a high-strength material in the early stage.

Research on the carbonation of cement paste mixed with additional cementitious materials is presented in [8]. Calcium silicate hydrates having various Ca/Si ratios from hydration reactions represent the main phases based on calcium, that reacts with CO_2. The work studied the accelerated carbonation mechanism of C-S-H phases with Ca/Si ratio between 0.66-2. It was experimentally found that all C-S-H phases were completely decomposed into $CaCO_3$ and SiO_2 gel after 3 days of accelerated carbonation applying. In this experiment, CaO and silica fume were used as raw materials, CaO being fresh produced by calcining $CaCO_3$ at temperatures of almost 1000 ºC. The materials in solid state together with the water were mixed, the solid/water ratio being 1:50. The synthesis process was performed in nitrogen atmosphere. After 14-28 days of reaction at room temperature, the samples were extracted in the form of slurry. Their drying took place below 35 ºC in vacuum drying chambers for 1 day. Then the specimens were kept into a desiccator at very low humidity. Their mechanical processing (grinding) in powder form was carried out before entering the carbonation room with a stable concentration of 3 % CO_2, temperature of 20 ºC, and humidity around 75 %. The duration of the carbonation process was varied between 0.5 hours and 7 days. The paper conclusion was that the C-S-H structure with Ca/Si ratio higher than 1.4 can be explained as a solid solution of C-S-H and $Ca(OH)_2$. The silicate in the final state is a silicate gel.

The potential of CO_2 storage in the concrete in early stage of hydration was also examined in other works [9-13].

The present paper aimed at the experimental production of high-strength concrete by applying the pre-curing technique of the fresh mix using sodium bicarbonate ($NaHCO_3$) as a partial substitute (between 7-21 wt. %) of ordinary Portland cement containing bi- and tri-calcium silicate (belite and alite) as main phases. The paper intends to contribute to the enrichment of knowledge regarding this new nonconventional method of early-age concrete curing combined with CO_2 sequestration by own experimental results.

2. METHODS AND MATERIALS

2.1 Methods

C-S-H carbonation was previously studied [14]. It is assimilated as "a complex process of decalcification-polymerization of C-S-H and formation of amorphous silica gel". A general form of the reaction is shown below:

$$xCaO \cdot SiO_2 \cdot H_2O + xCO_2 = xCaO \cdot CO_3 + SiO_2 \cdot H_2O + H_2O \quad (1)$$

where:

- $xCaO \cdot SiO_2 \cdot H_2O$ – calcium silicate hydrate (C-S-H), with x = 2 and 3;
- $CaO \cdot CO_3$ – calcium carbonate ($CaCO_3$);
- $SiO_2 \cdot H_2O$ – silica gel.

During carbonation, CO_2 enters the concrete pores and the main carbonation reaction takes place.

Pre-curing proposed in works highlighted in this study, was experimentally adopted to ensure adequate moisture content in the concrete samples, which through transforming would allow its penetration into the pores generated by CO_2. The different known curing methods are applied to extract the water content.

Mineral carbonation (or CO_2 mineralization) practically represents a storage process of CO_2 bound in form of carbonates. Carbonates are very low soluble in water and in terms of thermodynamics they are stable in normal atmospheric conditions, thus providing an excellent technical solution for permanent storage of this gaseous compound [11].

Early CO_2 binding method combines the advantage of CO_2 sequestration by its mineralization with the use of reaction elements ($CaCO_3$, SiO_2 gel or decalcified C-S-H phase) in order to increase the early-age strength of concrete [11].

The carbonation curing was proposed in construction materials industry since 50 years ago as

an alternative to steam curing, but the method was not considered interesting until recently, being associated with the actual requirements to reduce CO_2 emissions in atmosphere.

Early-age carbonation of concrete (in fresh state) is appreciated, because the calcium silicate phases easily react with CO_2 from the pores of the material.

According to the literature [4], in traditional Portland cement, calcium silicates slowly hydrate producing C-S-H and CNt in the form of nanoparticles that spread in the pore spaces, crystallizing. Theoretically, using sodium bicarbonate ($NaHCO_3$), the $CaCO_3$ ions existing in the areas of direct water/clinker contact (i.e. in hydration sites) lead to the transformation of CHt particles into amorphous CH, acting as a nucleation site for the C-S-H formation. Also, other subsequent transformations take place, generating the composite formed by $CaCO_3$ and C-S-H, accelerating the hydration process of clinker and favouring the increase of early-age mechanical strength. The advantage of carbonation in the fresh mixing stage of material is that the mineralized carbonates constitute a permanent storage place for CO_2 in the formed composite.

2.2 Materials

The experiment presented in this paper started from the adoption of a reference manufacturing recipe of a concrete based on Portland cement. The cement materials used were: ordinary Portland cement CEM I type (360 kg·m^{-3}), an addition of coal fly ash (4 kg·m^{-3}), and granulated blast furnace slag (5.5 kg·m^{-3}), so a total of 369.5 kg·m^{-3} cementitious materials. Supplementary cementitious material also added in the mentioned mixture was silica fume (nanomaterial with average particle size of 150 nm, resulting as a by-product of metallurgical industry) in very low proportions (about 4.5 kg·m^{-3}). It exhibits pozzolanic and cementitious properties as well as a combination of both properties [15].

The aggregate was composed of fine quartz sand (particles of maximum 1.7 mm) of 600 kg·m^{-3} and crushed granite stone (maximum 16 mm) of 850 kg·m^{-3}, i.e. a ratio between the two aggregate types of 0.7, which ensures satisfactory workability. The adopted amount of working water was 171 kg·m^{-3}, so that the water/cement ratio was between 0.51-0.60, adequate for obtaining the mechanical strength and durability of concrete. The reference concrete was subjected to the traditional curing process by keeping the fresh material (poured in the die) at 75 ºC for 24 hours, followed by keeping it outside the die at room temperature for 28 days before measuring the final specimen features.

Chemical composition of materials used in the experiment presented in this paper is shown in Table 1.

Table 1. Chemical composition of materials (wt. %)

Material	SiO_2	Al_2O_3	Fe_2O_3 (FeO)	CaO	MgO	Na_2O	K_2O	MnO	TiO_2	SO_3	LOI
CEM I type Portland cement	20.2	5.5	4.1	65.4	0.7	0.3	-	-	-	2.6	1.4
Coal fly ash	54.4	26.5	4.8	3.5	2.5	0.4	0.6	-	-	1.7	-
Blast furnace slag	37.4	6.4	6.9	39.9	3.5	0.1	0.2	2.2	-	-	-
Silica fume	92.6	0.9	2.0	1.0	1.0	-	1.3	0.1	0.3	0.3	5.0
Quartz sand	97.5	1.0	0.3	0.03		0.14		-	0.03	-	-
Granite sand	70-77	11-14	1-2 (1-3)	1.0	0.5-1	3-5	3-5	-	-	-	-

Experimental versions chosen by authors (Table 2) in which weight proportions between 7-21 % of ordinary Portland cement were successively replaced with sodium bicarbonate ($NaHCO_3$). Thus, the cement amount was decreased from 360 kg·m^{-3} to 284.4 kg·m^{-3}, while $NaHCO_3$ had successively the values of 25.2 kg·m^{-3} (7 %), 39.6 kg·m^{-3} (11 %), 54.0 kg·m^{-3} (15 %), and 75.6 kg·m^{-3} (21 %).

Table 2. Composition of experimental versions

Composition (kg·m^{-3})	Version			
	1	2	3	4
Portland cement	334.8	320.4	306.0	284.4
$NaHCO_3$	25.2	39.6	54.0	75.6
Coal fly ash	4.0	4.0	4.0	4.0
Blast furnace slag	5.5	5.5	5.5	5.5
Silica fume	4.5	4.5	4.5	4.5
Fine quartz sand	600	600	600	600
Crushed granite	850	850	850	850

stone				
Working water	171	171	171	171
Water/cement ratio	0.51	0.53	0.56	0.60

2.3 Techniques of investigating the sample features

The apparent density was determined by weighing the mass with an electronic balance relating this value to that of the specimen volume [16]. The porosity was measured using a vacuum saturation technique [17]. Compressive strength was identified with TA.XTplus Texture Analyzer and the flexural strength was measured according to SR EN ISO 1412:2000 [18]. Immersing method under water of sample for 24 hours (ASTM D570) was chosen to measure the water volume absorbed into the concrete body. The thermal conductivity was analyzed by the heat flow method (ASTM E1225-04) and the microstructural image of concrete samples was examined with ASONA 100X Zoom Smartphone Digital Microscope.

3. RESULTS AND DISCUSSION

3.1 Results

Thanks to the innovative technique adopted, the curing process was much advanced, taking place while the material was still fresh, i.e. during mixing and pouring into the mold and probably at the beginning of the time of its maintenance in the mold. The process took place at room temperature in a neutral nitrogen atmosphere at low pressure (0.7 bars or 70 kPa) without requiring additional thermal input and, even less, steam injection.

The samples manufactured in this experiment were compared with a reference concrete sample previously made according to a similar recipe except for $NaHCO_3$, whose mechanical characteristics were determined after 7 and 28 days.

The physical (apparent density, porosity, and water absorption) and thermal (thermal conductivity) characteristics of the samples manufactured in this experiment (versions 1-4) including also the previous results of the reference sample (noted with R) after 28 days are indicated in Table 3.

Table 3. Physical and thermal characteristics of concrete samples

Variant	Apparent density ($kg \cdot m^{-3}$)	Porosity (%)	Water absorption (vol. %)	Thermal conductivity ($W \cdot m^{-1} \cdot K^{-1}$)
1	2196	21.3	4.7	0.429
2	2203	21.0	4.5	0.433
3	2205	20.8	4.4	0.436
4	2208	20.6	4.4	0.440
R	2180	20.9	4.7	0.430

The mechanical characteristics (compressive strength and flexural strength) of samples obtained in this experiment were determined after 8 hours, 1 day, 7 days, and 28 days, while characteristics of the reference sample were measured after 7 and 28 days. The results are presented in Table 4.

Table 4. Compressive strength and flexural strength of concrete samples

Version	Compressive strength (MPa)				Flexural strength (MPa)			
	8 hours	1 day	7 days	28 days	8 hours	1 day	7 days	28 days
1	41.8	42.3	42.6	43.2	8.6	8.7	8.8	8.9
2	42.5	42.7	42.9	43.2	10.0	10.1	10.1	10.1
3	42.9	43.0	43.1	43.1	11.0	11.0	11.0	11.2
4	43.1	43.2	43.3	43.4	11.9	11.9	12.0	11.9
R	-	-	30.8	43.3	-	-	8.9	12.0

The data in Tables 3 and 4 are conclusive regarding the move of the usual curing period of fresh concrete from late-age (of the order of many days) to early-age, the process achieving even during mixing the concrete components and its casting. If the change in physical and thermal features of concrete specimens was not observed neither in experiments mentioned in the literature, nor in the current work, instead the obvious modification in the mechanical strength was remarked in the case of accelerating the carbonation process of calcium silicate hydrate (C-S-H) by introducing $NaHCO_3$ into the starting mixture.

Thus, according to Table 4, the compressive strength reached values very close to the maximum level since the mechanical tests performed after 8 hours. The experimental versions with lower additions of $NaHCO_3$ (25.2-39.6 $kg \cdot m^{-3}$) kept at room temperature (20-25 ºC) for up to 28 days recorded small increases in compressive strength from 41.8 to 43.2 MPa (in the case of version 1) and from 42.5 to 43.2 MPa (version 2). Instead, versions with higher additions of $NaHCO_3$ (54.0-75.6 $kg \cdot m^{-3}$) had very low, almost negligible increases, from 42.9 to 43.1 MPa (version 3) and from 43.1 to 43.4 MPa (version 4). By comparing with compressive strength values of the reference sample, it was found that after 7

days of traditional curing the concrete sample reached only 30.8 MPa, compared to the range of 42.6-43.3 MPa of the current experiment and after 28 days of curing it reached 43.3 MPa (i.e. almost identical to experimental sample 4).

Relatively similar situation was observed in the case of flexural strength. Thus, the highest values of the strength were reached before measurements carried out after 8 hours, the following determinations highlighting the almost constant maintenance of values. In the case of the reference sample, after the mechanical test performed at 7 days of curing, the flexural strength significantly increased from 8.9 to 12.0 MPa (after 28 days).

Appearance images of early-age concrete samples experimentally made in this experiment are shown in Figure 1.

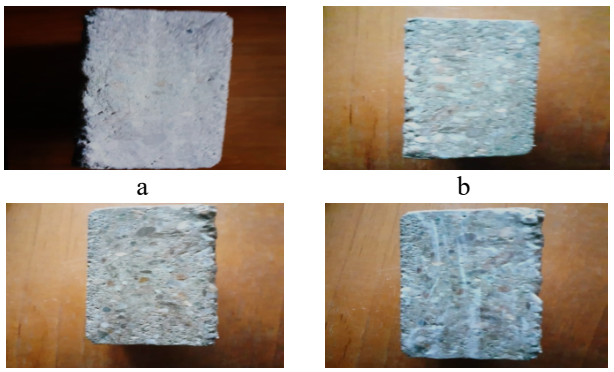

Figure 1. Appearance images of early-age cured concrete samples
a – version 1; b – version 2; c – version 3; d – version 4.

Microstructural aspect of early-age cured concrete samples is presented in Figure 2.

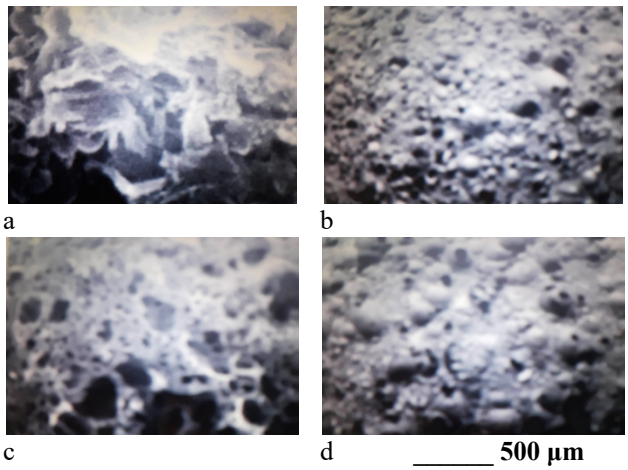

Figure 2. Microstructural appearance of early-age cured concrete samples
a – version 1; b – version 2; c – version 3; d – version 4.

3.2 Discussion

In the last years, research was initiated in the world for mineral carbonation (or CO_2 mineralization) as a permanent storing process of CO_2 bound in carbonates and reducing the emissions of this gaseous compound into the atmosphere. By hydrating calcium silicate from the composition of ordinary Portland cement, calcium silicate hydrate (C-S-H) and transition $Ca(OH)_2$ are created in the form of nanoparticles that enter the pore spaces of the fresh material, crystallizing. With the main aim of favouring the increase of early-age mechanical strength of concrete, the solution of introducing sodium bicarbonate into the mixture of cementitious materials was adopted, substituting between 7-21 % of the cement amount. Due to the bicarbonate, the $CaCO_3$ ions existing in the area of water-clinker direct contact lead to the transformation of the transition $Ca(OH)_2$ particles into an amorphous material acting as a nucleation site for the formation of calcium silicate hydrate. Also, other transformations generate a composite containing $CaCO_3$ and C-S-H, accelerating the hydration process of the clinker.

Thus, the early-age binding method of CO_2 in cement-based fresh concrete combines the advantage of CO_2 storage through its mineralization with the improvement of the early-age strength of concrete. This method, still in the research stage, could allow the continued use of cement as the basic binder of concrete in the actual conditions of the global ecological crisis, in which the manufacture of cement generates excessive CO_2 emissions.

The present work adopted the solution of using $NaHCO_3$ in the making process of cement-based concrete, performing experimental tests to enrich knowledge in this field. The results clearly confirmed the achievement of the high level of compressive strength in early-age, significantly reducing the need to apply traditional concrete curing techniques characterized by very long durations for the completion of hardening.

Preparing the material mixtures according to the amounts in Table 2 was carried out in the specialized laboratories of Metallurgical Research Institute Bucharest.

Physical, thermal, mechanical, and morphological features of specimens were determined in Metallurgical Research Institute and University “Politehnica” of Bucharest.

4. CONCLUSION

The work is part of the recent global research trend of early-age carbonation of calcium silicate hydrate (C-S-H), the main binding component of the Portland cement, simultaneously with CO_2 storage through its mineralization. Using $NaHCO_3$ (between 7-21 %) in the mixture of cementitious materials as a partial substitute for cement, the traditional curing process was advanced in an early-age period of the fresh mixture and the maximum value of the compressive strength was reached very quickly, being determined in the first mechanical tests after 8 hours. For the $NaHCO_3$ proportion of 21 %, the early-age strength reached 43.1 MPa, while the reference sample reached 30.8 MPa after 7 days and 43.3 MPa after 28 days.

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