Impact of the curing conditions and carbon dioxide ingress on heavyweight concrete

J Cepcianska¹, J Dragomirov¹, E Kuzielova¹,², M Zemlicka¹ and M T Palou¹,²

¹ Institute of Construction and Architecture, Slovak Academy of Sciences, Dubravská cesta 9, SK-845 03 Bratislava, Slovak Republic
² Faculty of Chemical and Food Technology, Slovak University of Technology, Radlinskeho 9, SK-812 37 Bratislava, Slovak Republic

Email: jana.cepcianska@savba.sk

Abstract. The present work investigates the influence of curing conditions on the mechanical and physical properties of heavyweight concrete. The prismatic bars of 40 mm × 40 mm × 160 mm dimension were cured in a climatic chamber (relative humidity 30%, average temperature 26°C), wet (100% of humidity, average room temperature 26°C) and CO₂ chamber-wet (relative humidity 90%, average temperature 50°C and average CO₂ concentration 20 %) conditions for 2, 7, 28 and 90 days. Density, compressive strength, dynamic modulus of elasticity, and longitudinal shrinkage were determined at different ages of curing. Mercury Intrusion Porosimetry was used to analyze and determine the influence of carbonation on pore structure evolution. Samples cured under CO₂- wet conditions showed a higher compressive strength (54.05, 66.83, 84.98, 96.35 MPa) compared to that of the samples exposed to wet (45.49, 65.87, 78.91, 93.80 MPa) and dry (39.62, 46.52, 48.45, 45.28 MPa) conditions at all ages. The dynamic modulus of elasticity of CO₂- wet cured samples (53.02, 51.48, 59.24, 67.60 GPa) was lower than that of samples cured in wet conditions (59.82, 66.76, 78.84, 80.27, GPa), but higher than that of dry-cured samples (45.74, 45.73, 43.91, 44.62 GPa). The density of the samples exposed to all curing conditions was higher than 3800 kg/m³. Carbonation led to a decrease in total porosity (from 10% to 20%) and an increase in density (from 320 to 390 kg/m³). Also, the time and curing conditions have strongly influenced the pore structure. The precipitation of calcium carbonate in the matrix of concrete and the acceleration of hydration reaction under wet conditions has led to a decrease in porosity.

1. Introduction
Although ordinary concrete is widely used as the main building material, heavyweight concrete plays a specific role of structural and functional material in the construction of nuclear power plants (NPPs), medical units, particle accelerator facilities or storage bunkers of nuclear wastes where construction is exposed to strong neutron or gamma-ray radiation [1–3]. Therefore, the development of heavyweight concrete, which can meet the functional and structure (mechanic) demands of a radiation shielding material, with proven low activation and high mechanical properties is highly required [3]. The manufacture of heavyweight concrete uses heavy natural aggregates such as barites or magnetite [4] or manufactured aggregates such as iron or lead shot. The heavy aggregates containing many heavy elements are crucial in improving concrete shielding properties and hence contribute greatly to the attenuation of photons and neutrons [5]. Generally, concrete with specific gravities higher that 2600 kg m⁻³ is called heavyweight concrete according to EN [6] and aggregates with specific gravity...
higher than 3000 kg.m$^{-3}$ are considered as heavyweight aggregates. Indeed, heavyweight concrete can undergo the same curing effects of temperatures and carbonation as ordinary concrete. It is manufactured using ordinary Portland cement or its blends as binder [1, 3–4]. Therefore, the hydration of cement phases in heavyweight concrete generates by the same manner different hydrous water-insoluble products with the capacity to blend the fillers, strengthen the structure and perform the durability of concrete over the time. The main products of cement hydration are calcium hydroxide Ca(OH)$_2$, calcium silicate hydrates C$_x$S$_y$H$_z$ (with different ratios), ettringite monosulfate or other calcium aluminate hydrates and in some cases calcium aluminosilicate hydrate. Calcium hydroxide Ca(OH)$_2$, calcium silicate hydrates C$_x$S$_y$H$_z$ are sensible to the action of carbon dioxide and produce calcium carbonate –phenomenon known as carbonation or carbon sequestration [7, 8].

In addition, unhydrated tricalcium silicate and dicalcium silicate (C$_3$S and C$_2$S) can also react with CO$_2$ in the presence of humidity to form calcium carbonate. The main carbonation reactions can be summarized as followed:

$$\text{CO}_2 + \text{Ca(OH)}_2 = \text{CaCO}_3 + \text{H}_2\text{O} \quad (1)$$
$$\text{CSH} + \text{CO}_2 = 2\text{CaCO}_3 + \text{SiO}_3\text{aq} + \text{H}_2\text{O} \quad (2)$$

where equation (2) describes total carbonation of C-S-H.

The carbonation mechanism, as reported by [8] can be divide into 8 stages: (1) diffusion of the gaseous CO$_2$(g) trough external layer surrounding the hardened concrete; (2) diffusion of CO$_2$(g) into the concrete pore solution; (3) solvation of CO$_3$ (aq); (4) hydration of CO$_2$(aq) to H$_2$CO$_3$(aq); (5) ionization of H$_2$CO$_3$ to H$^+$, HCO$_3^-$ and CO$_3^{2-}$; (6) dissolution of calcium containing phases to Ca$^{2+}$; (7) nucleation of CaCO$_3$(s) and (8) precipitation of solid phases.

Unfortunately, CO$_2$ lowers the pH of the alkaline environment surrounding steel reinforcements in concrete, this process reduces the level of a protective passive layer on the surface of steel reinforcement which makes it vulnerable for corrosion [9–11]. Moreover, in the presence of water excess, carbonation can produce carbonic acid and consequently a soluble Ca(HCO$_3$)$_2$ is formed.

$$\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3 \quad (3)$$
$$\text{H}_2\text{CO}_3 + \text{Ca(OH)}_2 = \text{CaCO}_3 + 2\text{H}_2\text{O} \quad (4)$$
$$\text{CaCO}_3 + \text{H}_2\text{CO}_3 = \text{Ca(HCO}_3)_2 \quad (5)$$

Ions of HCO$_3^-$ can then diffuse inward the sample and react there with the OH$^-$ ions to form the CaCO$_3$. Dissolution of CaCO$_3$ to form Ca$^{2+}$ and HCO$_3^-$ can appear only when pH value sufficiently drops. This process is supposed to take place only in the carbonation zone in the moist samples.

The effect of carbonation on the compressive strength of concrete was deeply studied by authors [10, 11]. Carbonation of fresh concrete can increase its compressive strength with time. Indeed, the ingress of CO$_2$ trough fresh concrete is more accentuated compared to hardened concrete due to the slow diffusion rate trough the dense microstructure.

### 1.1. Carbonation and shrinkage

Shrinkage can be classified into 4 groups depending on curing conditions [12, 13]: (1) plastic shrinkage, (2) autogeneous shrinkage/ self-shrinkage due to self-dessification, (3) drying shrinkage, and (4) carbonation shrinkage. Autogenous shrinkage is defined as a concrete volume contraction caused by the reduction of internal moisture due to consumption of water by internal chemical and structural reactions of the concrete components. It occurs without moisture transfer to the environment and contributes significantly to concrete cracking when the water–cement (w/c) ratio is less than 0.4. Self-shrinkage is caused by the loss of water when the water is consumed by cement hydration. Drying shrinkage occurs in environment with a lower relative humidity [12, 13]. As for shrinkage carbonation, it is above all the process resulting from chemical reactions and the precipitation of fine grains of calcium carbonate in a porous structure inside the concrete matrix and which induces the change in volume.
The main hypotheses proposed to explain the mechanism of CO\(_2\)-induced shrinkage were reported by [14, 15] who stated that, under partially saturated conditions, shrinkage is due to the pressure exerted by the gas on the dissolved molecules of Ca(OH)\(_2\) in highly "compressible fresh cement paste". Although this idea is refuted by other authors who claimed that this hypothesis is only valid for calcium hydroxide, it can be thought that this phenomenon may occur at an earlier hydration period in fresh concrete when partial pressure of CO\(_2\) can act on the component and cause the volume change.

The carbonation of C-S-H phases is hypothetically occurring via a topochemical mechanism in which no shrinkage was observed. Calcium carbonate is formed mainly in outer product regions as microcrystalline vaterite or calcite. Reardon et al. [14] are of the similar idea postulating that the carbonation of C-S-H occurs through decomposition by a pseudomorphic reaction and hence, does not affect the overall shrinkage. Contrary to this idea, author [15] has considered shrinkage of C-S-H through decalcification or loss of calcium by reaction. Indeed, carbonation remove calcium ions from C-S-H and changes the C/S ratio. When the ratio C/S is reduced below 1.2, the pastes shrank significantly and irreversibly. Authors of these findings called this phenomenon “decalcification shrinkage”, that is due to the structure changes in C–S–H at Ca/Si ∼ 1.2 and eventually to the decomposition of C–S–H into silica gel. That why blended cement paste exhibited greater decalcification shrinkage than the pure cement pastes due to its lower initial Ca/Si ratio for C–S–H gel [14].

### 1.2. Effect of carbonation on the pore structure of the hardening concrete

Another area of interesting research on concrete carbonation is the change in pore structure. The works of Claisse and Liu [16, 17] have studied the effect of carbonation on permeability and pore volume of carbonated concrete cured under wet and dry conditions and exposed in a carbonation chamber for up to 140 days. They pointed out that carbonation reduces the permeability and total porosity. It is evident that the precipitation of fine crystals of vaterite or aragonite in pore contributes to the reduction of total porosity and also the diffusion rate of gas, water and heat.

Although the carbonation reaction reduces the total porosity of OPC-based concretes, its significant impact on increase of the proportion of capillary pores (pore size greater than 30 nm) can be noticed on the pore size distribution. The increase in capillary porosity promotes the diffusivity of ions through the cement matrix. It has been reported that the specific surfaces of OPC paste samples are likely to decrease with an increase in the degree of carbonation [18].

It has been reported a strong correlation between the surface area measured by nitrogen BET and the degree of carbonation as determined by thermogravimetric analysis [18, 19].

The information on the carbonation shrinkage of heavyweight concrete is limited. Therefore, the present work was undertaken to understand the effect of three different curing regimes on physical and mechanical characteristics of heavyweight concrete. The material composition corresponds to concrete, but the measurements were done using standard for mortars. The experimental investigation includes long-term shrinkage, bulk density, compressive strength, dynamic modulus of elasticity and pore structure using mercury intrusion porosimetry (MIP).

## 2. Experimental

### 2.1. Used materials:

- Cement CEM I Extra 42.5 R; producer: Cement plant CRH a.s., Rohožník, Slovak Republic. Density: 3,143 kg/m\(^3\); specific surface: 4,341 cm\(^2\)/g
- Barite aggregate; producer: SABAR s.r.o., Markušovce, Slovak Republic. Density: 3 845 kg/m\(^3\)
- Cast iron aggregate; producer: IKB Slévárna Písečná s.r.o., Czech Republic. Grain size 22 and 32 mm. Density: 7 600 kg/m\(^3\)

### 2.2. Concrete setting retarder based on Lignosulfonates; producer:
Stachema Bratislava, a.s., Slovak Republic.
2.3. Concrete composition
Composition of prepared concrete samples is depicted in table 1, in which the designations for cement, superplasticizer and mixing water have been used.

| Material                      | Content |
|-------------------------------|---------|
| Barite                        | 55.06   |
| Cast Iron                     | 31.82   |
| Cement, CEM I                 | 9.06    |
| Superplasticizer, SP          | 0.12    |
| Water, W                      | 3.94    |
| Total                         | 100     |

2.4. Preparation of aggregate
Barite aggregate was crushed and sieved into different size fractions and remixed to obtain aggregate mixtures with defined particle size distribution falling into region of granulometric curves. Grain size composition was set to obtain grading curves of aggregates with largest grain of 16 mm.

| Fraction size [mm] | Aggregate grain-size composition [%] | Content in concrete [%] |
|-------------------|-------------------------------------|-------------------------|
| 0/0.063           | 0.25                                | 0.137                   |
| 0.063/0.125       | 0.125                               | 0.068                   |
| 0.125/0.25        | 0.068                               | 0.068                   |
| 0.25/0.5          | 6.070                               | 6.070                   |
| 0.5/1             | 2.510                               | 2.510                   |
| 1.0/2.0           | 8.369                               | 8.369                   |
| 2.0/4.0           | 5.379                               | 5.379                   |
| 4.0/8.0           | 12.074                              | 12.074                  |
| 8.0/16.0          | 17.93                               | 17.93                   |
| Total             | 55.054                              | 55.054                  |

2.5. Samples preparation and curing conditions
The manufacture of heavyweight concrete samples (trivial named EDU) was done in 3 phases: (1) the aggregates were mixed with a small quantity of water to fill the open pores before cement was added and the mixture was mixed in a semi-dry state during 5 min. (2) Then, half of the water and superplasticizer blend was added into the mixture which was then mixed for 8 min. (3) In the last stage, the remaining water and superplasticizer blend was added and mixed for 5 min. After mixing the concrete mixture was placed into the prism molds (40 × 40 × 160 mm). The molds then were covered with a plastic foil in order to avoid evaporation of surface water and were left to harden at a room temperature. After 24 h, the concretes specimens were demolded and subjected to three different curing regimes: climatic chamber (30 % of relative humidity, average temperature 26°C), humid curing (100 % r. h., average room temperature 26°C) and CO₂-chamber-wet (90 % r. h. at average temperature 50°C, average CO₂ concentration 20%) for 7, 28 and 90 days.
2.6. Test methods

- The compressive strength of specimens cured under different environments was measured according with the standard, EN 196-1 (2000) at the ages of 7, 28 and 90 days using a 1000 kN capacity mortar compression machine. The average compressive strength test results are calculated from six individual measurements.

- The dynamic modulus of elasticity was determined using Ultrasonic Meter Matest device. The measurement was performed on 40 × 40 × 160 mm prism specimens, which were afterwards used for the destructive compressive strength determination. The specimen was clamped at the middle section. The electromagnetic exciter (emitter) probe and the receiver probe were placed against each other on the two end faces of the sample at the mid-section. The exciter induced longitudinal pulses of sound into the concrete and the time the sound takes to travel from the transmitter probe to the receiver probe through the material was measured. Knowing the resonance frequency, the dynamic modulus was calculated using the following equation:

\[
E_d = 4. n^2 . L^2 . \rho . 10^{-15}
\]  

(6)

where \( E_d \) is the dynamic modulus of elasticity (GPa), \( n \) is resonant frequency (Hz), \( L \) is length of specimen (mm); \( \rho \) is the density of specimen (kg/m\(^3\)).

- Mercury intrusion porosimeter Quantachrome Poremaster 60GT (Quantachrome UK Limited) was used for the estimation of the curing environment on the pore structure parameters of the heavyweight concretes at 2, 7, 28 and 90 days. About 2 grams of samples without coarse aggregates used for the tests, were soaked in acetone and diethyl ether. The samples were dried in a vacuum atmosphere for 2 h before testing. The maximum applied pressure of mercury was 414 MPa, equivalent to a Washburn pore radius of 1.8 nm according to equation (7) [20]:

\[
r = -\frac{2\gamma \cos \theta}{P}
\]  

(7)

where \( r \) is the pore radius, \( \gamma \) is the surface tension of mercury (N/m), \( \theta \) is the contact angle between mercury and the solid materials and \( P \) is the applied pressure (Washburn, 1921, Carlos, 1998).

3. Results and Discussion

3.1. Density

The density of heavyweight concrete after 2, 7, 28 and 90 days are shown in figure 1. The bulk density of EDU heavyweight concrete is higher than 3900 kg.m\(^{-3}\). The influence of curing environment has a negligible influence on bulk density because of high density aggregates. The negligible variation of bulk density with time and curing conditions resulted from measurement errors as it can be observed with the intensity of standard deviations.

![Figure 1](image_url)
3.2. **Compressive strength**

The compressive strength of hardened EDU heavyweight concrete cured under the three different environments is shown in figure 2. At all time of curing, compressive strength is found dependent on environment. Under dry curing conditions, the development of compression strength is negligible due to loss of water by evaporation. It is a general rule that the compressive strength strongly depends on the degree of hydration which runs only in the presence of water. 90-day compressive strength exceeding 45 MPa increased only by 21% compared to the 2-day one.

![Figure 2. Compressive strength of heavyweight concrete EDU (dried samples).](image)

The compressive strength evolved positively over time marked by a significant difference values measured at 2, 7, 28 and 90 days under wet and CO\(_2\)-wet curing environments (figure 2). It is evident that under these conditions the hydration of the cement proceeded and hence increased the compressive strength. 90-day compressive strength increased by about 106% and 78% for samples cured under wet and CO\(_2\)-wet curing respectively in comparison with the samples cured for 2 days. Nevertheless, it should be noted that the values of compressive strength of samples cured under CO\(_2\)-wet conditions are higher than that of samples exposed to wet environment. This difference is higher at the beginning than at the later time. However, it should be noted that this beneficial effect of CO\(_2\) on the mechanical properties of OPC based systems is observed when the fresh concrete mix is subjected to carbonation. During this phase, CO\(_2\) under pressure diffuses easily into the concrete bulk and supports the homogeneous formation of calcium carbonate in concrete matrix. The precipitation of calcium carbonate in micro and macropore contributes to the reduction of total porosity and hence, to the increase of compressive strength [13, 15, 21]. When the hardened (or matured) concrete samples are subjected to carbonation, the CO\(_2\) penetration depth is mostly limited to the outer layer of the samples because of the slow diffusion rate through the dense microstructure. In such condition, the increase in strength of OPC-based systems due to the carbonation is not significant. These findings were reported by also [7]. The enhanced compressive strength can be explained by the degree of hydration. Indeed, it was reported [22–23] that carbonation accelerates the hydration of tricalcium silicate. Hydration is a complex physical and chemical process. The consumption of calcium hydroxide by carbonation can induce acceleration of C\(_3\)S dissolution to keep the alkalinity of liquid phase. In the meantime, carbonation can decalcify CSH producing poorly calcium silicate gel with a lower content of calcium.
3.3. Dynamic modulus of elasticity (DME)

The DME of prepared samples cured in dry environment increased very slightly from the beginning to 90 days. DME is an important characteristic of concrete and can be used to compute the dynamic Young’s Modulus (E) [4]. The higher the value of DME, the stiffer concrete is. Also, it characterizes the heterogeneity of structure such as aggregate, water content, air voids, transition zone, and porosity. It depends on concrete age, curing regime and material composition. As it can be observed in figure 3, DME increased significantly in wet and CO$_2$-wet curing regimes. Unfortunately, the values of DME of A EDU heavyweight concrete cured in CO$_2$-wet environment, are slightly lower than that of EDU cured in wet environment. It can be expected that the precipitation of huge amount of calcium carbonate crystals may reduce the stiffness of concrete. An increase of DME depends on the concrete maturity which is directly dependent of degree of hydration. It can be related to the shrinkage also.

3.4. Shrinkage characteristics

The typical shrinkage strain behavior of the three EDU heavyweight concretes is plotted in figure 4. Samples underwent volume changes because of physical and chemical interaction with the internal and external environment. It is worth noting that the curing conditions significantly affected the magnitude of concrete shrinkage because the flux of moisture out of the pore structure of concrete is mainly related to the restraining effect of concrete maturity. As dry curing ran at r. h. below 30% humidity, it is evident that drying shrinkage occurred. The mechanism of dry shrinkage has been reported as the effect of capillary stress when water evaporates from the capillary pores. Then, the tension is transferred to the walls of pores causing thus drying shrinkage [12]. Wet cured and dry cured heavyweight concrete samples have opposite behavior. While in dry conditions, samples showed important shrinkage due to evaporation of water, in wet conditions samples expanded slightly. In these conditions, the formation of new hydration products was supported by 100% humidity which keep almost constant quantity of water in the concrete matrix to ensure further hydration. A low content of water in the concrete matrix leads to an excessively dry condition for the ionization of CO$_2$ and prevents the dissolution of calcium hydroxide, while a high humidity inhibits the diffusion of dissolved CO$_2$ through open surface pores. This is why the carbonation tests on mortars or concrete are carried out in conditions of humidity not exceeding 70%. The course of CO$_2$-wet cured samples is interesting. The carbonation shrinkage is subject to different interpretations. During the first hours of curing, Ca(OH)$_2$ submitted to the pressure of CO$_2$ diffusion can be compressed leading to intensive shrinkage. The shrinkage is observed during the first 11 days. In the meantime, CSH was exposed to the action of CO$_2$ and its decalcification leads to an excessively dry condition. The decalcification of CSH structure causes the volume change known as “decalcification shrinkage”, predominantly at the earlier period of hydration. Acceleration of C$_3$S hydration and decalcification of CSH are controversial and this phenomenon can explain lower
shrinkage of CO₂-wet cured heavyweight concrete compared to wet cured one. On the other hand, crystallization of calcium carbonate can compensate the effect of carbonation shrinkage.

![Figure 4. Continual shrinkage of EDU heavyweight concrete.](image)

3.5. Pore structure analysis

The visual evolution of concrete carbonation observed by application of phenolphthalein solution on samples of age 90-days is depicted in figure 5. Practically, total volume carbonation as consequence of CO₂ diffusion into the sample was observed on the sample stored in CO₂ chamber. Samples stored in a wet environment and in climatic chamber showed no signs of carbonation.

![Figure 5. Carbonation test. From the left concrete sample cured in climatic chamber, wet and CO₂ chamber.](image)

The present work prefers to interpret the influence of carbonation on concrete through in-depth analysis of MIP results. Characteristics, such as total porosity with interparticle and intraparticle porosity components, pore size distribution, bulk density, total surface area were determined. These parameters have provided therefore the relevant information regarding the influence of curing environments on the pore structure of heavyweight concrete.

Total surface area is the sum of surface area of all pores and voids filled up to pressure P. Total porosity is the sum of interparticle porosity (spaces between particles) and intraparticle porosity (within particles).

These pore parameters result from the following equations (Carlos A 1998 26) [25]:

\[
\text{Interparticle porosity (\%)} = 100 \frac{V_p}{V_b} \quad (8)
\]

\[
\text{Intraparticle porosity (\%)} = 100 \frac{V_t - V_p}{V_b} \quad (9)
\]

\[
\text{Mercury intrusion (total) porosity (\%)} = 100 \frac{V_t}{V_b} \quad (10)
\]

where \(V_b\) is the bulk volume of the sample, \(V_p\) is the volume of mercury intruded up to the interparticle filling limit and \(V_t\) is the total volume of mercury intruded up to the maximum pressure.
The classification of pores proposed by Metha and Monteirio [25] was used to divide the pores into particular categories according to their diameter as follows: gel pores (< 4.5 nm), mesopores (4.5–50 nm), middle capillary pores (50–10^2 nm), large capillary pores (10^2–10^4 nm), macropores (> 10^4 nm). The characteristics of pore structure are reported in table 3. It is evident that the total porosity depended on curing conditions and on the curing time. Dry curing caused a substantial increase in total porosity when compared with wet and CO_2-wet curing due to the lack of water for advanced hydration.

**Table 3. Characteristics of pore structure of EDU heavyweight concrete.**

| Curing condition | Dry curing | CO_2-Wet curing | Wet curing |
|------------------|------------|-----------------|------------|
| Curing period[day] | 2  7  28  90 | 2  7  28  90 | 2  7  28  90 |
| Total porosity[%] | 10.766  10.02  9.147  9.062 | 7.028  7.694  6.144  4.102 | 6.366  5.37  6.1933  4.057 |
| Interparticle porosity[%] | 0.96  0.633  0.683  0.58 | 0.378  1.098  0.915  0.851 | 0.815  0.72  0.8305  0.857 |
| Intraparticle porosity[%] | 9.806  9.387  8.514  8.482 | 6.65  6.596  5.229  3.251 | 5.551  4.65  5.3628  3.2 |
| Total surface Area [m^2/g] | 1.488  1.283  1.299  1.303 | 3.107  3.254  3.483  3.856 | 0.951  0.928  2.560  1.287 |
| Bulk density[g/cm^3] | 3.909  3.981  3.895  3.785 | 3.955  4.299  4.430  4.345 | 4.004  4.064  4.227  4.337 |

In such conditions, water evaporated and let empty space or voids. Since hydration cannot continue, the initial large pores are not filled with hydrated products. The higher total porosity explains the lower value of compressive strength and DME of EDU heavyweight concretes cured under dry conditions. Surprisingly, the total porosity of samples cured in CO_2-wet condition is slightly higher than that of samples exposed to wet conditions. The main influence of carbonation can be observed with the values of total surface area. The explanation of this finding escape still to our understanding, but it could be related to the presence of gel pores as reported by pore size distribution (PSD) at figure 6. However, it can be seen that the intraparticle porosity which is the main component of the total porosity is higher in samples CO_2-wet cured than that cured in wet conditions.

3.6. **Influence of curing in dry curing regime**

Other relevant demonstration of the influence of curing conditions and curing time on pore structure is illustrated by pore size distribution and cumulative pore volume shown in figures 5–10. The cumulative pore volume expresses the summation of mercury volume intruded into the pores and interparticle voids versus the applied pressure. These two characteristics are uniform with samples cured in dry conditions (figure 5).

The total porosity is constituted of middle capillary pores (50–10^2 nm) and large capillary pores (10^2–10^4 nm). After 7 days, one noted a negligible change in pore structure. This stagnation is due to the lack of water responsible for hydration of cement phases to produce nano size CSH with possibility to fill large pores. If he concentration of CO_2 in air is negligible, therefore its effect on carbonation of sample is also negligible.
Figure 6. Characteristics of pore structure of dry cured EDU heavyweight concrete.

3.7. Influence of curing in CO\textsubscript{2}-wet curing regime

When cured in wet and CO\textsubscript{2}-wet conditions, the curve of PSD (figure 6) showed the presence of gel pores (< 4.5 nm) and mesopores (4.5–50 nm) represented by curves having the form of a zigzag. The presence of gel pores resulted from the formation of CSH. The pore size distribution in ranged between gel pore, middle capillary pores (50–10\textsuperscript{2} nm) with a negligible portion of large capillary pores (10\textsuperscript{3}–10\textsuperscript{4} nm).

The presence of macro pores is not observed. The volume of intruded mercury is reduced and we observe an increase of middle capillary pores (50–10\textsuperscript{2} nm) after 2, 7, 28 days of curing.

Figure 7. Characteristics of pore structure of CO\textsubscript{2}-wet cured EDU heavyweight concrete.

3.8. Influence of curing in wet curing regime

The wet curing conditions are known as standard ones for evaluation of the mechanical and physical properties of mortars and concrete.
Figure 8. Characteristics of pore structure of wet cured EDU heavyweight concrete.

These conditions prevent the samples from drying out and ensure the continuity of the hydration which is responsible for the development of mechanical and physical properties including pore structure. The important presence of middle capillary pores (50–10^2 nm) illustrates the degree of hydration under these conditions (figure 8). One can observe the presence of gel pores (< 4.5 nm) and mesopores (4.5–50 nm) from the age of 28 days, while these pores are found in samples cured under CO₂-wet from the beginning.

3.9. Influence of curing environment on the pore characteristics

Figures 9–12 illustrate the effect of different curing environment on the pore structure of EDU heavyweight concrete at 2, 7, 28 and 90 days. These figures clearly show the effect of conditions on pore size distribution and volume intruded. Dry conditions are distinguished by the high values of volume intruded and the positioning of PSD in the region of micropores with important portion of capillary pores. As previously reported, the stagnation of the pore structure development is caused by the lack of water.

3.10. Influence of 2-day curing regimes

Figure 9. Characteristics of pore structure of EDU heavyweight concrete after 2-day curing.

After 2 day-curing, one notes the displacement of PSD towards finer pore structure with apparition of gel pore in sample CO₂-cured (figure 9). The assumption of CO₂ penetration into the depth of the material is usually limited to the carbonation front. CO₂ resp. CO₃²⁻ reaction with calcium hydroxide in the alkaline environment of the cement matrix is relatively fast and shifted to the side of the reaction products. The formation of these products can lead to reduction of pore sizes [27].
3.11. Influence of 7-day curing regimes

The 7-day curing under different environments did not bring about any substantial change compared with 2-day curing except that the portion of gel pores increased in CO₂-cured samples. Sample cured under wet conditions had the lowest volume intruded, a slight displacement of PSD towards finer structure including mostly the middle capillary pores (50–10² nm) and large capillary pores (10³–10⁴ nm), but the presence of gel pore was not detected (figure 10).

![Figure 10. Characteristics of pore structure of EDU heavyweight concrete after 7-day curing.](image)

3.12. Influence of 28-day curing regimes

The main difference with curing conditions was observed in figure 10 with the apparition and extension of gel pore portion. The hydration and carbonation effect was evidenced by pore refinement of samples cured under wet and CO₂-wet conditions. At this stage, volume intruded of both samples was reduced compared to dry cured sample. The refinement was possible thanks to the progress in hydration and carbonation. The compressive strength of the samples in this time also increased (figures 1, 2).

![Figure 11. Characteristics of pore structure of EDU heavyweight concrete after 28-day curing.](image)

3.13. Influence of 90-day curing regimes

90-day curing brought a significant change in pore structure. The porosity of wet and CO₂-wet cured EDU heavyweight concretes decreased. The values of total volume intruded for both samples are similar. Also, a drastic reduction of the intensity of PSD peak of samples cured under wet and CO₂-wet conditions was observed. In the meantime, the portion of gel pore increased. The 90-day curing increased the portion of gel both in wet and CO₂-cured samples. Hydration continued causing the formation of a higher amount of CSH (figure 12).
Figure 12. Characteristics of pore structure of EDU heavyweight concrete after 90-day curing.

4. Conclusion
Heavyweight concrete was manufactured and the prepared samples were subjected to curing in three different curing environments: dry curing, CO$_2$-wet curing and wet curing. The effect of carbonation on mechanical and physical properties of samples was studied. Curing in dry condition did not ensure the increase of the compressive strength and dynamic modulus of elasticity at later time. CO$_2$-wet curing together with wet curing has a positive impact on compressive strength increase. Ultimately, wet treatment results in the highest sample strengths. Also the dynamic modulus of samples cured in CO$_2$-wet and wet environment reached higher values in comparison with samples cured in climatic chamber. The pore structure has not been refined. Curing of samples in the CO$_2$-wet environment has led to the increase in compressive strength, even compared to the standard curing conditions. It affected the shrinkage, specific surface and the portion of gel pore from the beginning. The wet condition (standard) has refined the pores structure with the apparition of gel pore after 28 days.

Acknowledgement
This work was supported by courtesy of APVV-19-0490, APVV-15-0631, Slovak Grant Agency VEGA No. 2/0032/21 and 2/0017/21.

References
[1] Ouda A 2015 Development of high performance heavy density concrete using different aggregates for Gamma-Ray shielding Prog.Nucl. Energy 79 pp 48–55
[2] Kyoungsoo P, Hyung_tae K, Tae-Hyun K and Eunso Ch 2016 Effect of neutron irradiation on response of reinforced concrete members for nuclear power plants. Nuclear Engineering and Design 310 pp 15–26
[3] Dragomirová J and Palou MT 2019 Development of High-Compressive Heavyweight Concrete Based on Portland Cement and Supplementary Cementitious Materials Materials Science Forum 955 pp 44–49
[4] Dragomirová J, Palou M T, Kuzielová E, Žemlička M, Novotný R and Gméling K 2020 Optimization of cementitious composite for heavyweight concrete preparation using conduction calorimetry Jour. Therm. Anal. Calorim 142 pp 255–266
[5] Dragomirová J, Palou M T, Gméling K, Szilágyi V, Harsányi I and Szentmiklóst L 2019 Design of heavyweight concrete used in radiation protection based on complete NAA, PGAA and XRF results; activation and physical properties In Brittle Matrix Composites 12 Proc. 12th Int. Symp. Brittle Matrix Composites (Warsaw : Institute of Fundamental Technological Research) pp 195–210
[6] STN EN 206+Ai: 2017 Concrete_ Part 1: Concrete. Specification, performance, production and conformity STN (Bratislava)
[7] Groves G W, Rodway D I and Richardson I G 1990 The carbonation of hardened cement pastes Adv. Cem. Res. 3 pp 117–125
[8] Jang J, Kim G M, Kim H J and Lee H K 2016 Review on recent advances in CO$_2$ utilization and sequestration technologies in cement-based materials Constr. Build. Mater. 127 pp 762–773
[9] Fernández B M, Simons S J R, Hills C D and Carey P J 2004 A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO₂ Journal of Hazardous Materials 112 pp 193–205

[10] Liu R, Jiang L, Xu J, Xiong C and Song Z 2014 Influence of carbonation on chloride induced reinforcement corrosion in simulated concrete pore solutions Constr. Build. Mater. 56 pp 16–20 (Online http://dx.doi.org/10.1016/j.conbuildmat.2014.01.030)

[11] Marangu J M, Thiong’o J K and Wachira J M 2019 Review of Carbonation Resistance in Hydrated Cement Based Materials, Review Article Hindawi Journal of Chemistry ID 8489671 pp 1–6 (Online https://doi.org/10.1155/2019/8489671)

[12] Mushtaq S M, Siddique R, Goyal S and Kaur K 2021 Experimental studies and drying shrinkage prediction model for concrete containing waste foundry sand Cleaner Engineering and Technology 2 pp 100071

[13] Cheung A K F and Leung C K Y 2011 Shrinkage reduction of high strength fiber reinforced cementitious composites (HSFRCC) with various water-to-binder ratios Cement & Concrete Composites 33 pp 661–667

[14] Reardon J, James E and Abouchar B R 1989 High pressure carbonation of cementitious grout Cem. Concr. Res. 19 pp 385–399

[15] Chen J J, Thomas J J and Jennings H M 2006 Decalcification shrinkage of cement paste Cem. Concr. Res. 36 pp 801–809 (Online http://dx.doi.org/10.1016/j.cemconres.2005.11.003)

[16] Claisse P A, Elsayad H I and Shaaban I G 1999 Permeability and pore volume of carbonated concrete ACI Mater. J. 96 pp 378–381

[17] Liu L, Jiang J, Xu C and Xiong Z S 2014 Influence of carbonation on chloride induced reinforcement corrosion in simulated concrete pore solutions Constr. Build. Mater. 56 pp 16–20 (Online http://dx.doi.org/10.1016/j.conbuildmat.2014.01.030)

[18] Ngala V T and Page C L 1997 Effects of carbonation on pore structure and diffusional properties of hydrated cement pastes Cem. Concr. Res. 27 pp 995–1007

[19] Philajavaraa S E 1968 Some results of the effect of carbonation on the porosity and pore size distribution of cement paste Mater. Constr. pp 521–526

[20] Washburn E W 1921 Note on a Method of Determining the Distribution of Pore Sizes in a Porous Material. Proc. Nation. Acad. Sc. USA(PNAS) 7 (4) pp 115–116 (Online https://doi.org/10.1073/pnas.7.4.115)

[21] Zhenghu L, Yinchuan G, Zhihui C, Aiqin S, Xiao Q, Jingyu Y and Ming Z 2019 Research on shrinkage development and fracture properties of internal curing pavement concrete based on humidity compensation Constr. Build. Mater. 203 pp 417–43

[22] Berger R L, Young J F and Leung K 1972 Acceleration of hydration of calcium silicates by carbon dioxide treatment Nat. Phys. Sci. 240 pp 16–18

[23] Young J F, Berger R L and Breese J 1974 Accelerated curing of compacted calcium silicate mortars on exposure to CO₂ J. Am. Ceram. Soc. 57 pp 394–397 (Online http://dx.doi.org/10.1111/j.1151-2916.1974.tb11420.x)

[24] Sevelsted T F and Skibsted J 2015 Carbonation of C–S–H and C–A–S–H samples studied by 13C, 27Al and 29Si MAS NMR spectroscopy Cem. Concr. Res. 71 pp 56–65 (Online http://dx.doi.org/10.1016/j.cemconres.2015.01.019)

[25] Carlos A. León y León 1998 New perspectives in mercury porosimetry Advances in Colloid and Interface Science 76 –77 pp 341–372 (Online https://www.sciencedirect.com/journal/al/advances-in-hydrocolloid-interf-sciencescience/vol/76/suppl/C)

[26] Mehta P K and Monteiro P J 2017 Concrete Microstructure, Properties and Materials (McGraw-Hill Education: New York, NY, USA) (Online accessengineeringlibrary.com)

[27] In-Seok Yoon and Chun-Ho Chang 2020 Time Evolution of CO₂ Diffusivity of Carbonated Concrete Appl. Sci. 10 pp 8910