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THE CARBONATION OF AUTOCLAVED AERATED CONCRETE

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ABSTRACT

During the long-term investigation of the physical properties of autoclaved aerated concrete (AAC) in the indoor environment with changing relative humidity and temperature the significant increase of the AAC density was found. It was proved that the increase of the density was a consequence of carbonation process. For the investigated types of the AAC the ultimate increase of density was proportional to initial dry density of the AAC. It was found as well that relative volumes of the micropores (with radius from 3.5 nm to 7500 nm) of the investigated types of the AAC are proportional to their dry densities. The simulation of the time courses of density increase due to carbonation based on solution of modified diffusion equation was done. In spite of using simplifications (constant value of CO_2 diffusion coefficient, neglecting the relative humidity changes), the calculated time courses coincided sufficiently with the measured ones. © *1997 Elsevier Science Ltd*

Introduction

The carbonation of the PC based materials is generally modelled by the calculation of carbonation depth. The calculation of carbonation depth is based on an assumption that the carbonating material can be considered to be semi-infinite medium. The another approach suitable for simulation of the carbonation in the elements of complex form (edge, infinite plate, rectangular paralellepiped, cylinder), based on the analytical solution of the modified diffusion equation can be applied in the cases when the mean moisture content of the material is steady and the parameters of the carbonation can be considered to be constant. This approach has been applied for the case of the AAC and it has been experimentally verified on specimens of rectangular paralellepiped form.

Model of Carbonation

Carbonation is a chemical reaction controlled by carbon dioxide diffusion. This follows from the fact that the chemical reaction by which the immobilized reactant is formed proceeds very rapidly compared with the diffusion process. In the case when carbonation is present the usual equation of diffusion has to be modified by addition of the term expressing the amount of CO_2 consumed by chemical reaction and it becomes [1]:

$$\partial(\varepsilon.C)/\partial t + \partial S/\partial t = \mathrm{div}\,(D_e\,\mathrm{grad}C) \qquad (1)$$

where ε is porosity [-], C is CO_2 concentration in pores of carbonating material [$kg.m^{-3}$], t is time [s], S is amount of CO_2 consumed by chemical reaction per unit volume of the carbonating material [$kg.m^{-3}$], D_e is effective diffusion coefficient [$m^2.s^{-1}$].

Effective Diffusion Coefficient. The effective diffusion coefficient is expressed by the relation:

$$D_e = D/\mu \qquad (2)$$

where D is the diffusion coefficient of CO_2, μ is the CO_2 diffusion resistance factor [-]. In air $D = 1.4.10^{-5}\,m^2.s^{-1}$ at the temperature 0°C and normal atmospheric pressure [2]. The value of CO_2 diffusion resistance factor is not equal to the water vapour diffusion resistance factor value. For example in [3] the measured D_e value of aerated concrete, at RH less than 60%, is $6.10^{-7}\,m^2.s^{-1}$, consequently the μ value is about 23, that means about 3 times higher than the water vapour diffusion resistance factor. The value of effective diffusion coefficient depends on the open porosity of the material and on its moisture content. The carbonation leads to changes in microstructure and decrease of the porosity and consequently to the decrease of the effective diffusion coefficient value. This effect is important in PC based materials with fine pore structure (pore radius ≤ 500 nm), for example in hydrated cement pastes (HCP) with low value of W/C ($W/C \leq 0.5$) [4], but can be neglected in aerated concretes, total porosity of which is in the range 70-80% and most of this porosity is concentrated in macropores. On the other hand the decrease of the CO_2 effective diffusion coefficient of aerated concrete with the increase of its moisture content is significant [3].

Concentration of Carbon Dioxide Consumed by Chemical Reaction. From the fact that during the carbonation the chemical reaction proceeds very rapidly compared with the diffusion process the existence of local equilibrium between the free and immobilised CO_2 can be assumed. In the simplest case the relation between the concentration S of carbon dioxide consumed by chemical reaction and concentration C of carbon dioxide free to diffusion can be assumed as linear [1]:

$$S = R\,.\,C \qquad (3)$$

Providing that the initial CO_2 concentration in pores of carbonating material is equal to 0 and CO_2 concentration in the ambient air is constant, the parameter R can be expressed as:

$$R = \Delta\rho_M / C_a \qquad (4)$$

where $\Delta\rho_M$ is the maximum possible density increase of material caused by carbonation [$kg.m^{-3}$], C_a is carbon dioxide concentration in ambient air [$kg.m^{-3}$].

The relation (3) expresses the fact that the equilibrium between CO_2 concentration in ambient air and CO_2 concentration in the pores of carbonating material will take place when maximum possible density increase is achieved.

Maximum Possible Density Increase Caused by Carbonation. The density increase can be expressed by the amount of CO_2 required for carbonation of unit volume of material. The evaluation of $\Delta\rho_M$ is based on determination of maximum amount of CaO available for carbonation. According to this approach in the case of PC based materials the $\Delta\rho_M$ is given by equation:

$$\Delta\rho_M = A_c \cdot \frac{A_{CaO}}{A_c} \cdot \frac{CO_2}{CaO} \cdot K \tag{5}$$

where A_c is the amount of portland cement in the concrete or mortar [kg.m^{-3}], A_{CaO}/A_c is amount of CaO per unit of cement [kg/kg] (it is about 0.60 - 0.65 in the case of portland cement [5]), CO_2, CaO are molecular masses of these compounds [kg], K is coefficient expressing the degree of carbonation and possible water loss accompanying carbonation. Its value is in the range 0.59 - 0.87 [5].

In case of the AAC the relation for maximum density increase is expressed similarly:

$$\Delta\rho_M = \rho \cdot \frac{A_{CaO}}{\rho} \cdot \frac{CO_2}{CaO} \cdot K \tag{6}$$

where A_{CaO} / ρ is the amount of CaO per density of AAC. The values of K for the AAC are lower than in the case of PC based materials.

Solution of Modified Diffusion Equation. The hereinafter presented solutions of equation (1) are valid if the carbonation can be considered a continuous process, that means necessary conditions of the carbonation process (necessary moisture content of material, availability of $Ca(OH)_2$ capable of being carbonated) are fulfilled.

Substituting the relation (3) to equation (1), provided that the effective diffusion coefficient is constant and taking into account that the value of ε is negligible compared with the value of R we obtain equation:

$$\partial C/\partial t = (D_e /R).\text{div grad } C \tag{7}$$

In one-dimensional case the equation (7) is:

$$\partial C/\partial t = (D_e /R)).\partial^2 C/\partial x^2 \tag{8}$$

The solution of modified diffusion equation for two special cases - semi-infinite medium and rectangular parallelepiped will be presented. The solution for semi-infinite medium is interesting from practical point of view, because it is a good approximation for description of the carbonation in a wall, the solution for rectangular parallelepiped was applied for simulation of the carbonation process in the tested specimens.

For semi-infinite medium, providing that surface concentration of CO_2 is constant:

$$C = C_a, \qquad x = 0, \qquad t > 0 \tag{9}$$

at intial condition:

$$C = 0, \qquad x > 0, \qquad t = 0, \tag{10}$$

a solution of equation (8) is [1] :

$$C(x,t) = C_a.\left(1 - \mathrm{erf}\frac{x}{2.\sqrt{D_e \cdot t/R}}\right) \tag{11}$$

where erf is the error function.

Substituting the assumption $C(x,t) = 0.29.C_a$ into the equation (11) the well known relation for carbonation depth is obtained:

$$d = \sqrt{\frac{2.D_e.t}{R}} \tag{12}$$

The density of the CO_2 diffusion flow q_m to the semi-infinite medium is expressed by relation:

$$q_m = \left(D_e.\frac{\partial C}{\partial x}\right)_{x=0} = C_a \cdot \frac{\sqrt{D_e.R}}{\sqrt{\pi.t}} \tag{13}$$

and the achieved increase of mass per unit of surface area after time τ is given by [1] :

$$\Delta m(\tau) = \int_0^\tau q_m dt = 2.C_a.\sqrt{\frac{D_e.R.\tau}{\pi}} \tag{14}$$

In the case of a rectangular parallelepiped with edges of lengths 2a, 2b, 2c, provided that the surface CO_2 concentration is constant:

$$C(-a,y,z) = C(a,y,z) = C(x,-b,z) = C(x,b,z) = C(x,y,-c) = C(x,y,c) = C_a \qquad t > 0, \tag{15}$$

and initial condition is as follows:

$$C = 0, \qquad -a < x < a, \quad -b < y < b, \quad -c < z < c \qquad t = 0, \tag{16}$$

the solution of the equation (7) is [1] :

$$C(x,y,z,t) = C_a \cdot \left\{1 - \frac{64}{\pi^3}\sum_{i=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{(-1)^{i+m+n}}{(2i+1)\cdot(2m+1)\cdot(2n+1)}\cdot\cos\frac{(2i+1)\pi x}{2a}\cdot\cos\frac{(2m+1)\pi y}{2b}\cdot\right.$$

$$\left.\cos\frac{(2n+1)\pi z}{2c}\cdot\exp\left[-t\frac{D_e\pi^2}{R}\left(\frac{(2i+1)^2}{4a^2}+\frac{(2m+1)^2}{4b^2}+\frac{(2n+1)^2}{4c^2}\right)\right]\right\} \tag{17}$$

The relation expressing the density increase due to carbonation after time t is obtained by integrating the product of the expression for concentration (17) multiplied by the R over the whole volume of parallelepiped [1] :

$$\Delta\rho = \Delta\rho_M \cdot \left\{1 - \frac{512}{\pi^6} \sum_{i=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{1}{(2i+1)^2 \cdot (2m+1)^2 \cdot (2n+1)^2} \cdot \exp \left[-t \frac{D_e \pi^2}{R} \left(\frac{(2i+1)^2}{4a^2} + \frac{(2m+1)^2}{4b^2} + \frac{(2n+1)^2}{4c^2} \right) \right] \right\} \tag{18}$$

For long times, that means in the cases when the following relation for Fourier number Fo is fulfilled:

$$\mathrm{Fo} = t \cdot \frac{D_e}{R \cdot a^2} > \mathrm{Fo}_m \tag{19}$$

sufficiently accurate results are obtained by retaining only the first terms in each of the series of the the expressions (17) and (18). The relation (18) can be then rewritten as follows:

$$\Delta\rho = \Delta\rho_M \left\{ 1 - \frac{512}{\pi^6} \exp\left[-t \cdot \frac{D_e \cdot \pi^2}{R} \cdot \left(\frac{1}{4a^2} + \frac{1}{4b^2} + \frac{1}{4c^2} \right) \right] \right\} \tag{20}$$

The value of Fo_m is dependent on the ratio of the parallelepiped dimensions. For example if $a = b = c$, then $\mathrm{Fo}_m = 0.21$ and if $a = b$, $c = 4a$, then $\mathrm{Fo}_m = 0.37$.

For small times the more convenient solution of equation (7) is according to [1] :

$$C(x,y,z,t) = C_a \sum_{i=0}^{\infty} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} (-1)^{i+m+n} \cdot \left[\operatorname{erfc} \frac{(2i+1) \cdot a - x}{2 \cdot \sqrt{t \cdot D_e / R}} + \operatorname{erfc} \frac{(2i+1) \cdot a + x}{2 \cdot \sqrt{t \cdot D_e / R}} \right] \cdot \left[\operatorname{erfc} \frac{(2m+1) \cdot b - y}{2 \cdot \sqrt{t \cdot D_e / R}} + \operatorname{erfc} \frac{(2m+1) \cdot \cdot b - y}{2 \cdot \sqrt{t \cdot D_e / R}} \right] \cdot \left[\operatorname{erfc} \frac{(2n+1) \cdot c - z}{2 \cdot \sqrt{t \cdot D_e / R}} + \operatorname{erfc} \frac{(2n+1) \cdot c + z}{2 \cdot \sqrt{t \cdot D_e / R}} \right] \tag{21}$$

and the corresponding relation expressing the carbonation density increase after time t can be written:

$$\Delta\rho = \Delta\rho_M \cdot \left[1 - \left(1 - 2\sqrt{\frac{D_e \cdot t}{\pi \cdot R \cdot a^2}} + 4\sqrt{\frac{D_e \cdot t}{R \cdot a^2}} \cdot \sum_{i=0}^{\infty} (-1)^i \operatorname{ierfc} \frac{1}{\sqrt{D_e \cdot t / R \cdot a^2}} \right) \cdot \right.$$

$$\left(1-2\sqrt{\frac{D_e\cdot t}{\pi\cdot R\cdot b^2}}+4\sqrt{\frac{D_e\cdot t}{R\cdot b^2}}\cdot\sum_{m=0}^{\infty}(-1)^m\,\mathrm{ierfc}\frac{1}{\sqrt{D_e\cdot t/R\cdot b^2}}\right)\cdot$$

$$\left.\left(1-2\sqrt{\frac{D_e\cdot t}{\pi\cdot R\cdot c^2}}+4\sqrt{\frac{D_e\cdot t}{R\cdot c^2}}\cdot\sum_{n=0}^{\infty}(-1)^n\,\mathrm{ierfc}\frac{1}{\sqrt{D_e\cdot t/R\cdot c^2}}\right)\right] \qquad (22)$$

If the condition $Fo < Fo_m$ is fullfiled, the relation (22) can be simplified to :

$$\Delta\rho=\Delta\rho_M\cdot\left[1-\left(1-2\sqrt{\frac{D_e\cdot t}{\pi\cdot R\cdot a^2}}\right)\cdot\left(1-2\sqrt{\frac{D_e\cdot t}{\pi\cdot R\cdot b^2}}\right)\cdot\left(1-2\sqrt{\frac{D_e\cdot t}{\pi\cdot R\cdot c^2}}\right)\right] \qquad (23)$$

In practice the value of Fo_m can be estimated from the condition that difference between the $\Delta\rho$ calculated according to the equation (20) and the $\Delta\rho$ calculated according to the equation (23) is equal to 0. At that time the $Fo_m = Fo$.

Experimental Results

Two sets of AAC SIPOREX (sand) specimens with the mean dry densities 529 $kg.m^{-3}$ and 545 $kg.m^{-3}$ and one set of AAC CALSILOX (fly ash) specimens with the mean dry density 573 $kg.m^{-3}$ were tested during the 9 years period (from 1987 to 1996). Number of the specimens in each set was 8. The dimensions of the specimens were $0.15 \times 0.15 \times 0.6$ m. The specimens were exposed in the laboratory with air temperature varying from 17°C to 25°C and air relative humidity varying from 22 to 80% during the test. The process of the AAC density changes consisted of three phases: During the first phase excessive water loss took place. The density of the AAC with initial water content 27% rapidly dropped down during about two months. During the second phase a small increase of density caused by the water vapour sorption up to equilibrium moisture content could be observed. The third phase was defined by significant increase of the AAC density in the state of equilibrium moisture content (2.5 - 4.0% per mass). At the end of the experiment, the phenolphthalein pH test was done, which confirmed decrease of pH along the whole cross- section of the exposed specimens in comparison with the non-exposed ones. The results of the experiment were compared with experimental data of Novotný, Plos [6], achieved for AAC CALSILOX (fly ash) specimens with dry density 545 $kg.m^{-3}$ and AAC CALSILOX (sand) specimens with dry density 590 $kg.m^{-3}$ with dimensions $0.1 \times 0.1 \times 0.4$ m. The parameters of all examined types of AAC are in Table 1.

The measured time courses of the density of AAC specimens during the third phase were compared with the calculated ones where the increases of density were calculated according to relations (20) and (23). The comparison of the measured and calculated courses of density is shown in Fig. 1.

TABLE 1

Initial Dry Densities, CaO Content, Maximum Density Increase $\Delta\rho_M$ and Degree of Carbonation K of the AAC Specimens

Type of AAC	dry density [kg/m^3]	Amount of CaO [%]	Amount of CaO [kg/m^3]	Density increase $\Delta\rho_M$ [kg/m^3]	K
SIPOREX (sand)	529	28	148	7	0.06
	545	28	153	17	0.14
CALSILOX (fly ash)	545	17.6	96	10	0.13
	573	17.6	101	31	0.39
CALSILOX (sand)	590	24.3	143	38	0.34

Comparison of the Simulation Results with Experimental Data

Maximum Possible Density Increase Caused by Carbonation. In order to verify applicability of relations (5) or (6) for PC based materials the dependance of measured $\Delta\rho_M$ values on CaO amount for the AACs (by the authors and by [6]), concretes [8], hardened cement

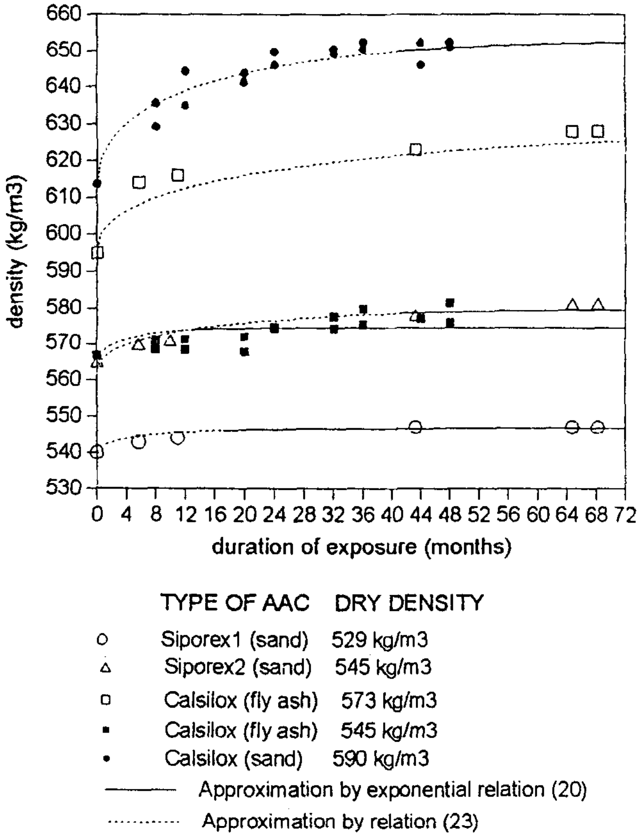

FIG. 1.

The measured and calculated time courses of the AAC specimens densities.

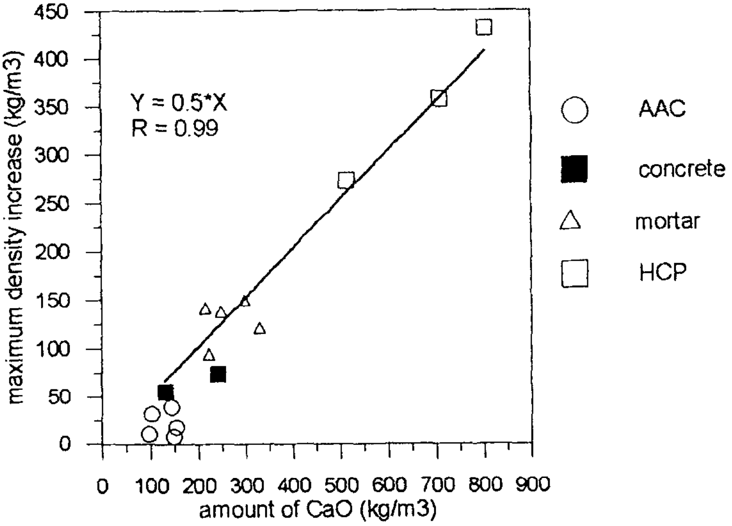

FIG. 2.
Experimentally determined relation between the maximum density increase $\Delta\rho_M$ and the CaO amount for PC based materials in comparison with data for the AACs.

pastes (HCP) [4] and mortars [9] are compared in Fig. 2. As can be seen from the Fig. 2 the linear relation between $\Delta\rho_M$ and amount of CaO is acceptable for all materials with exception of the AAC. The adequate degree of carbonation resulting from relation (5) is K = 0.63. In comparison with the other materials in the case of the AAC the lower portion of available CaO is spent for carbonation (Table 1). The linear relation between density increase $\Delta\rho_M$ and initial dry density of the AAC was found. (Table 1, Fig. 3).

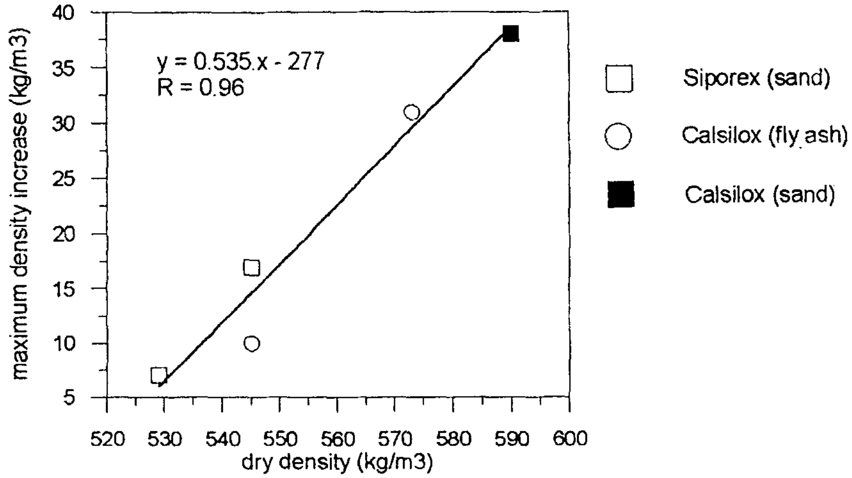

FIG. 3.
Experimentally determined relation between the maximum density increase $\Delta\rho_M$ and initial dry density for AAC specimens.

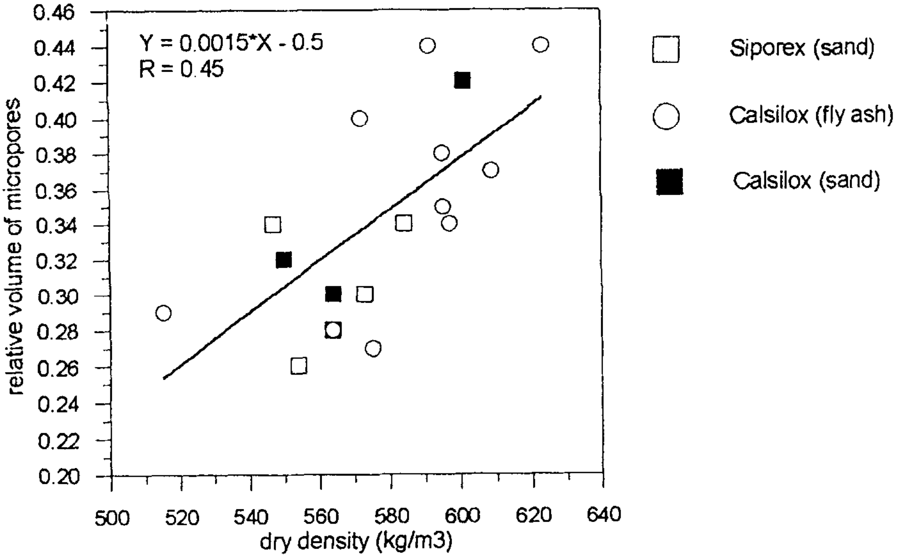

FIG. 4.

The relation beween the relative volume of micropores of the investigated types of AAC and their densities.

Time Course of the Carbonation Density Increase. The comparison between the density increase $\Delta\rho$ (according to relations (20) and (23)) and the experimental results obtained for five types of AAC is shown in Fig. 1.

The same values of $D_e = 6.10^{-7}\ m^2.s^{-1}$ [3] and C_a = 600 mg .m^{-3} were used in all calculations. The used values of $\Delta\rho_M$ (Table 1) were determined from measurements. The calculated time courses of carbonation density increase coincided satisfactorily with the measured ones. In the case of CALSILOX specimens with initial dry density 573 kg.m^{-3} the carbonation process had not been fully finished. Consequently the found maximum value of density increase was not ultimate and therefore the calculated time course of density increase is slightly underestimated.

Discussion

The values of the AAC maximum density increase obtained from the experiment were analysed from the aspect of their correlation with the CaO content. The measured maximum density increase was not a function of only CaO content (Table 1). It was found that the degree of carbonation K for the AAC tested specimens had lower values than for the PC based materials and the apparent correlation between the degree of carbonation and initial AAC density (Fig. 3, Table 1) was observed. With the aim to find the possible relation between the degree of carbonation and the pore structure of the AAC a set of the mercury intrusion porosimetry measurements for the investigated types of AAC [10] have been analysed. The found correlation between the relative volumes of micropores (with radius from 3.5 nm to 7500 nm) of the investigated types of AAC and their densities (Fig. 4) could explain the apparent correlation between the initial density and maximum density increase. From the mentioned it follows that degree of carbonation of the AACs is dominantly influenced by their pore structure and the equilibrium moisture content adequate to it. However the analysed sets of the specimens were not satisfactorily representative from the aspect of the ranges of their densities, relative volumes of micropores and they were tested at only one level of the ambient relative humidity. Therefore the correlations between the degree of carbonation, relative volume of micropores and equilibrium moisture content of the AAC should be verified for wider range of these parameters.

The comparison of the measured and calculated time courses of the AAC density gave a good coincidence. Fluctuations of the measured values from the calculated ones were caused by the fluctuations in the moisture content (about ±2 kg/m^3 in measurements of the authors [7]) of the specimens during the year. In the simulation some simplifications were used: CO_2 diffusion coefficient was considered constant and the possible effects of the varying ambient relative humidity were neglected. From the aspect of the carbonation and its influence on the porestructure of the AAC the CO_2 diffusion coefficient could be used constant, because the changes of the total porosity, which is significant from the aspect of diffusion are negligible. As the changing moisture content of the specimens did not reach the values adequate to relative humidities over 60% the decrease of the CO_2 diffusion coefficient of the AAC caused by the increase of moisture content was negligible. Similarly the periods with the relative humidities below 30% did not cause significant decrease of specimens moisture content and their influence on carbonation process could be neglected. This simplification may not be correct in the cases of the smaller specimens. Generally the simultaneous simulation of the time courses of the moisture content distribution in the specimen is necessary.

Conclusions

The long-term measurements of the AAC density increase due to carbonation were carried out in the laboratory conditions. The results of the measurements have been compared with simulation based on the analytical solution of modified diffusion equation (1).

It was confirmed that it is possible to simulate time courses of the carbonation process by analytical solution of modified diffusion equation for the bodies of simple geometrical forms.

The correctness of the results is dependent on the correctness of the carbonation describing parameters, i.e.: CO_2 diffusion coefficient, maximum increase of density, CO_2 concentration. The moisture content is a significant factor influencing the values of these parameters but in the cases when the mean moisture content of AAC is steady the parameters of the carbonation can be considered to be constant. The changes of the AAC microstructure due to carbonation are not important for the CO_2 diffusion coefficient value.

In the case of equal CaO content in the AACs with different densities the maximum increase of the density for particular AAC is determined by its degree of carbonation. The degree of AAC carbonation is apparently dependent on its density, which is explained by the proportionality between the density and relative volume of micropores of the AAC.

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References

1. Crank J., The Mathematics of Diffusion. Second Edition, Oxford University Press, Oxford 1975.
2. Klopfer H., Wassertransport durch Diffusion in Festsoffen, Bauverlag GmbH Wiesbaden und Berlin 1974.
3. Houst Y., Wittmann F.H., The Diffusion of Carbon Dioxide and Oxygen in Aerated Concrete, in Proceedings of the second International Colloquium of Material Science and Restoration, pp. 629-634, Technische Academie Esslingen, Ostfildern, 1986.
4. Houst Y., The role of moisture in the Carbonation of Cementious Materials, International Journal for Restoration of Buildings and Monuments, 2 (1), 49-66 (1996).
5. Schiessl P., Zur Frage der zulässigen Rissbreite und der erfoderlichen Betondeckung im stahlbetonbau unter besonderer Berücksichtigung der Karbonatisierung des Betons. Deutscher Ausschluss für Stahlbeton, Heft 255. Berlin 1976.
6. Novotný J., Plos J., Tests of aerated concrete durability in environment with various stage of air pollution. (In Czech) Stavivo 7-8 , 284-285 (1987).
7. Hanečka K., Koronthályová O., Matiašovský P., Changes of mass and density of AAC. Building Research Journal SAV, 44 (1), 31-41 (1996).
8. Müller A., Sickert G., Determination of the Carbonation Resistance of Concrete on the Basis of its Capillarity and Microstructure. Concrete Precasting and Technology, 11, 70-88 (1995).
9. Ying-yu L., Q.-D. Wu., The Mechanism of Carbonation of Mortars and the Dependence of Carbonation on Pore Structure, in Concrete Durability-Katharine and Bryant Mather International Conference, SP 100, Vol 2, 1915-1943, American Concrete Institute, Detroit, 1987.
10. Jambor J., Bágel' L'., Determination of basic parameters of AAC specimens. (In Slovak) Institute of Construction and Architecture Report. Bratislava 1984.