

## TECHNOLOGY AND ORGANIZATION OF CONSTRUCTION

UDC 691.328.001.66

*Mordvinian State University*

*Ph.D. in Engineering. Assoc. prof. of Dept. of Building Structures*

*P. I. Novichkov*

*Russia, Saransk, tel.: + 7(8342)47-40-19;*

*e-mail: bogatovad@list.ru*

P. I. Novichkov

### THE TYPES OF LIMITATIONS ON CARBONIZATION INTENSITY IN CONCRETE

**Problem statement.** Taking into consideration the effect of moisture conditions of concrete by introducing empirical coefficients which are not justified theoretically and experimentally does not provide physical understanding of the influence of concrete structure and its moisture conditions.

**Results and conclusions.** It is suggested to differentiate the inflow of the gas mixture to concrete into effusion and diffusion components with respect to the diameter of capillaries. The expressions for estimation of their contribution to the general flow depending on moisture content are given.

**Keywords:** concrete, differential and integral porosity, carbonization, diffusion, effusion.

**Introduction.** During the process of hardening of cement stone or concrete complex ramified system of randomly located capillaries from  $10^{-2}$  to  $10^{-7}$  cm and individual pores of diameter from  $10^{-2}$  to 0.5 cm is formed as a result of chemical and physical-mechanical properties. The type of location of pores and capillaries in concrete and their differential distribution by size are closely related to the mechanism of the transfer of external gas-like aggressive medium deep into porous solid. Depending on the size of capillaries and pores, the transfer of external medium might occur in pores which are not filled with condensed moisture in the form of molecular flow or effu-

sion at sizes of capillaries  $r < 1 \times 10^{-5}$  cm or in the form of viscous motion or diffusion at  $r > 1 \times 10^{-5}$  cm. In capillaries filled with water, the transfer of external gas-like medium is possible in solution in response to diffusion motion. The type of transfer is liquid transfer in liquid.

The permeability of concrete as a porous material to external gas medium, or gas permeability, is characterized by the transfer coefficient, or diffusion coefficient [1, 2, 3]. Effective coefficient of diffusion [1, 2] accumulates all possible types of transfer without differentiation of the contribution of each type to the final value of the coefficient. In terms of prediction of life expectancy of the structures, such approach is justified.

At the same time, in terms of directed formation of the structure of concrete and cement stone, integral value of the coefficient of transfer in the form of effective coefficient not always allows to conduct valid quantitative and qualitative assessment of the measures which are being performed. This is due to the fact that concrete permeability depends on many factors including structure parameters, integral volume of pores and capillaries, their differential distribution by size, environment humidity, concrete humidity, etc.

The procedure suggested in [1] uses the following equation to calculate of effective coefficient of diffusion  $\text{CO}_2$  at concrete carbonization  $D'$ :

$$D' = \frac{m_0 x^2}{2C_0 \tau}, \quad (1)$$

where  $x$  is the depth of carbonization defined with the use of indicator by changing hydrogen index pH;  $C_0$  is the concentration  $\text{CO}_2$  in environment;  $\tau$  is the life expectancy, or observation period;  $m_0$  is the reaction capacity of concrete, that is, the volume of carbonic acid gas absorbed by unit of volume of carbonized concrete at normal temperature and pressure

The structure of expression (1) used to define effective coefficient of diffusion and diffusion parameters testifies that  $D'$  is not a value of carbonic acid gas transfer, but, most probably, is the rate of the progress of concrete carbonization.

In other words, the value of effective coefficient of diffusion combines parameters characterizing two processes — the process of carbonic acid gas transfer to the front of reaction and the process of chemical interaction of carbonic acid gas with alkaline components of cement stone in reaction zone. The prerequisite for choosing this procedure to define effective coefficient of diffusion is acceptance of assumption of diffusion limitation on the rates of the processes. This assumption implies that diffusion transfer of carbonic acid gas from external medium to the front of reaction is the slowest process among other processes involving concrete carbonization. At the same time in expression (1), apart from reaction volume of concrete, neither concrete struc-

ture related to the integral volume of pores and their differential distribution by size, nor relative concrete humidity. In this connection, coefficient  $D'$  in the form (1) should be interpreted as coefficient of movement of the front of reaction in concrete carbonization.

The influence of humidity and temperature conditions of environment in [1] is proposed to consider with the use of empirical coefficient:

- 1 — for structures inside dry heated premises;
- 0.5 — for protected from precipitation external structures in the centre of European part of Russia;
- 0,2—0,3 — for external structures not protected from precipitation according to the humidity conditions.

Generally (see, for example, [1]), at present we do not have an opportunity to take into consideration the effect of conditions of structure interaction with environment on the kinetics of concrete carbonization differentially. Hence, taking into consideration the effect of moisture conditions of concrete by introducing empirical coefficients which are not justified theoretically and experimentally does not provide physical understanding of the influence of concrete structure and its moisture conditions.

From our point of view, physically, it is more justified to differentiate integral system of pores into microcapillaries with radius of capillaries  $r < 1 \times 10^{-5}$  cm and into macrocapillaries with radius  $r > 1 \times 10^{-5}$  cm when determining coefficient of gas transfer which can be named as effective coefficient of mass potential transfer. Let us denote the effective coefficient of diffusion by  $D$  and find total scalar density  $j$  of gas flow transported through the surface of capillary-porous body of area  $A$  in a unit of time using the first Fick's law:

$$j = DA \frac{dc}{dx}. \quad (2)$$

Scalar value of total gas flow  $j$  at isothermal conditions will be made up of gas flow transported under the effect of effusion  $J_{eff}$  through microcapillaries and of gas flow transported by diffusion  $J_{diff}$  through macrocapillaries:

$$J = J_{eff} + J_{diff}. \quad (3)$$

For polycapillary-porous body, total pore areas falls on area  $A$  of body surface contacting with environment, or porosity, are equal, respectively:

- for microcapillaries

$$A_{eff} = \int_{r_{min}}^r f(r) dr; \quad (4)$$

- for macrocapillaries

$$\Pi_{diff} = \int_r^{r_{max}} f(r) dr, \quad (5)$$

where

$$r = 1 \times 10^{-5} \text{ cm}$$

is the boundary value of the capillary radius in their separation into microcapillaries and macrocapillaries;  $r_{min}$  is the minimum value of microcapillary radius;  $r_{max}$  is the maximum value of microcapillary radius;  $f(r)$  is the pore size differential distribution curve.

Scalar value of gas flow transported under the effect of effusion with consideration for [4] is equal to

$$J_{eff} = \frac{8}{3} \sqrt{\frac{RT}{2\pi M}} r \Pi_{eff} \frac{dc}{dx}. \quad (6)$$

In expression (6), the gradient of partial pressure  $\frac{dP}{dx}$  is substituted for active gas in gas mixture in relation to Clapeyron-Mendeleev equation:

$$P = \frac{m}{V} \frac{RT}{M}, \quad (7)$$

where  $m$  is the mass of carbon dioxide in gas mixture;  $M$  is the molecular mass of carbon dioxide;  $V$  is the mixture volume;  $R$  is the universal gas constant;  $T$  is the absolute temperature.

The scalar value of the density of gas flow transported by diffusion and determined by Fick's first law, with consideration for (5), is equal to

$$J_{diff} = D_{diff} \Pi_{diff} \frac{dc}{dx}. \quad (8)$$

By substituting values of gas flows from (2), (6) and (8) in (3) instead of gas flows and performing appropriate transformation, we obtain the value of effective coefficient of diffusion  $D$ . It is equal to

$$D = \frac{\Pi_{diff}}{A} D_{diff} \left[ 1 + \frac{8}{3} \sqrt{\frac{RT}{2\pi M}} \frac{1}{D_{diff}} \frac{(\Pi_{eff} / A)}{(\Pi_{diff} / A)} r \right], \quad (9)$$

where  $\Pi_{eff}/A$ ,  $\Pi_{diff}/A$  are relative areas of microcapillaries and macrocapillaries on the surface of the body which contact with environment.

The second member in brackets in expression (9) indicates the part of gas flow transported by effusion with reference to diffusion component. If this member is equal to zero, the flow of transported gas inside porous body will be fully controlled by macrocapillar component of porous system of concrete. As is seen from (9), this may happen if  $r \cdot \Pi_{eff}$  approaches zero.

$$r \cdot \Pi_{eff} = \int_{r_{min}}^r r \cdot f(r) dr \rightarrow 0. \quad (10)$$

Reduction of microcapillar component of concrete porous structure can occur in two cases.

At first, this may happen in the course of interaction of chemically responsive components of cement stone or fillers with penetrating environment. As a results of this interaction, insoluble products of reaction with zero porosity fill microcapillaries.

At second, this may happen at full wetting of microcapillaries by condensed moisture. As a result, the transfer of gas-like products is possible only in dissolved form on the model of liquid transfer in liquid. In transferring dissolved gas in the form of liquid in liquid, diffusion coefficient will be four orders less than gas coefficient in gas. In this case, gas flow transported in dissolved form on the model of liquid transfer in liquid will be equal to zero.

When it is considered that reaction products forming as a result of reaction of concrete components with gas environment will not be absolutely dense at standard temperature conditions and will have certain final porosity, it can stated that decrease and increase of effusion component in total flow of transported gas will depends only on condensed moisture content in porous body microcapillaries.

It is obvious that condensed moisture content in microcapillaries depends on relative pressure of water vapor over the water meniscus or on relative equilibrium concrete moisture. The relationship between capillary radius and relative pressure of water vapor over the meniscus at full wetting is given in [4].

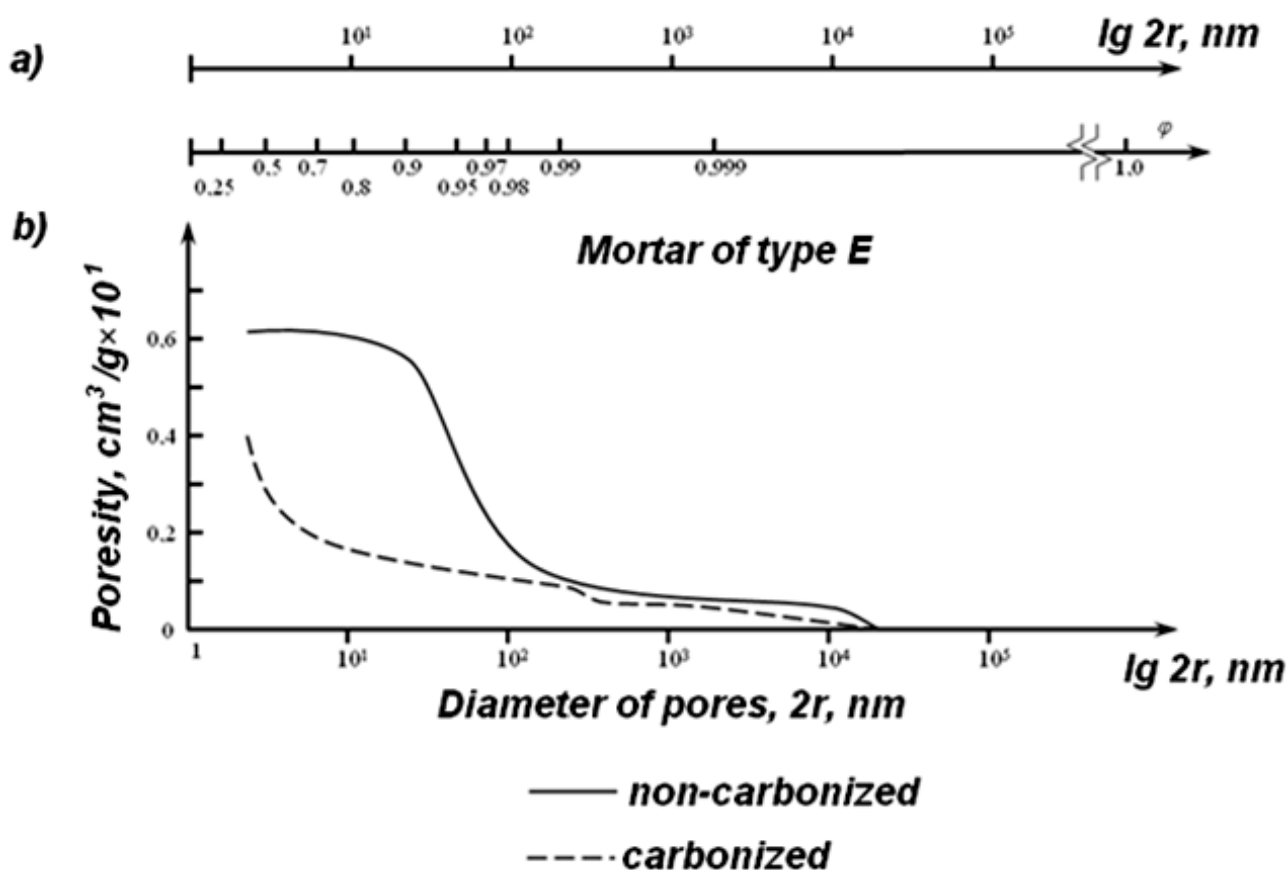
Let us calculate the change in effusion and diffusion components of gas flows depending on condensed moisture content in capillaries as relative equilibrium concrete moisture increases. To do this, let us use data on volumes of pores of cement/sand mortar 1/2 obtained with the use of mercury porometer (see Fig. 1b) [2]. We assume that material is isotropic.

In studying the influence of relative equilibrium moisture on the change in diffusion and effusion components of gas flow inside porous body, we adopt the value of gra-

dient of concentration  $\frac{dc}{dx}$  to be equal for both components of the flow. From (6) and (8) we obtain the expressions for scalar values of relative densities of the flows:

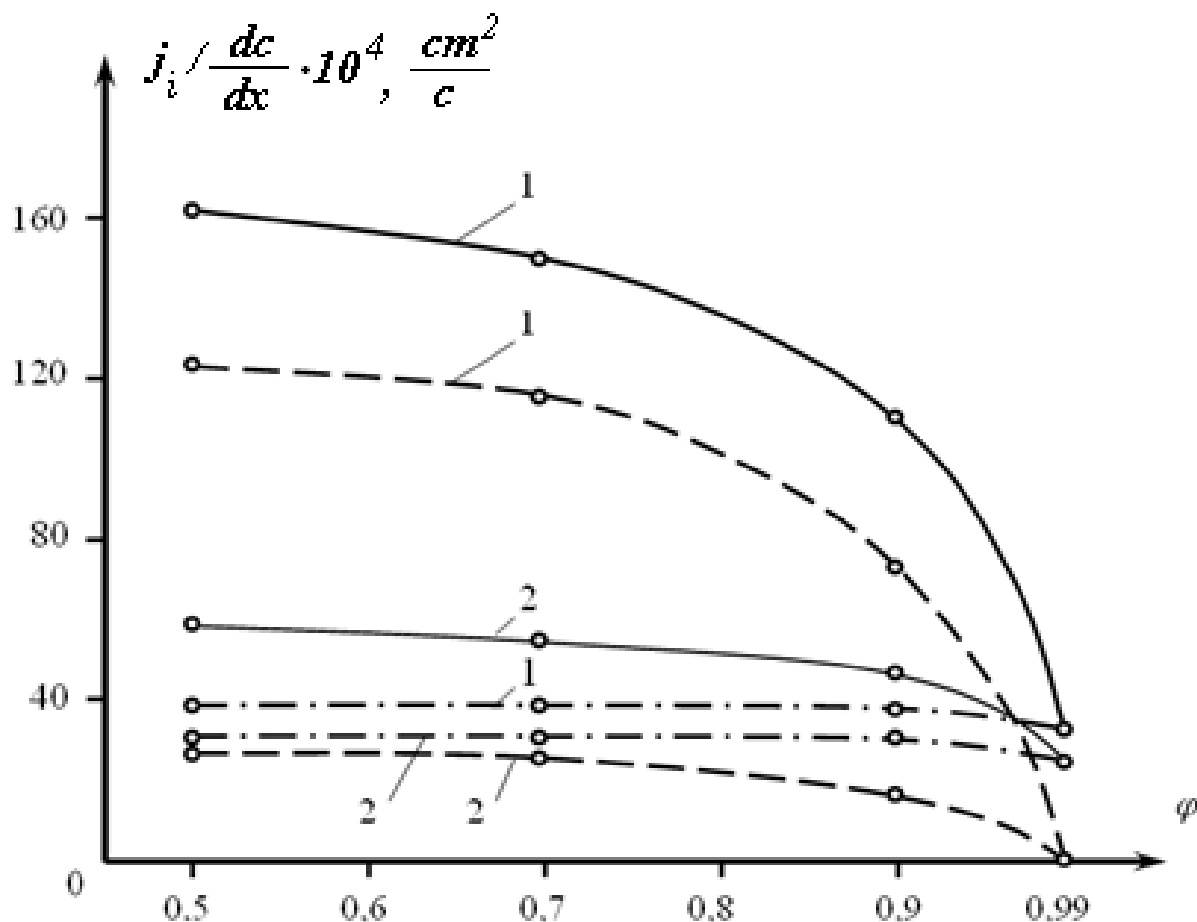
$$\frac{j_{eff}}{\frac{dc}{dx}} = \frac{8}{3} \sqrt{\frac{RT}{2\pi M}} \Pi_{eff} \cdot r; \quad (11)$$

$$\frac{j_{diff}}{\frac{dc}{dx}} = D_{diff} \Pi_{diff}. \quad (12)$$



**Fig. 1.** The relationship between capillary radius:  
a) and relative water pressure at which full wetting of capillary of radius  $r$  occurs [4];  
b) and pore distribution in uncarbonized and carbonized solutions [2]

Fig. 2 shows curves of change of diffusion and effusion components of relative carbon dioxide flows in relation to relative pressure of water vapor inside the mortar.



**Fig. 2.** The change in relative densities of the flows of carbonic acid gas arriving at mortar, in relation to relative humidity:  
 ——— total relative density of the flow of carbonic acid gas at the surface of cement-sand mortar;  
 - · - - diffusion component; - - - effusion component;  
 1 – before carbonization of mortar; 2 – after carbonization of mortar

In determining the value of diffusion flow of carbonic acid gas, value of  $D_{diff}$  is taken equal to  $0.16 \text{ cm}^2/\text{sec}$ , as for coefficient of gas diffusion in gas at  $T = 293 \text{ K}$  ( $20^\circ \text{C}$ ). The area of microcapillaries  $\Pi_{eff}$  and macrocapillaries  $\Pi_{diff}$ , as well as radius of capillaries  $r_i$  was determined from Fig. 1b with consideration for the film of condensed moisture. The width of the film was taken from [4] in relation to the relative pressure of water vapor in mortar  $\varphi$ .

Components of the flow were determined for two states of the mortar.

State 1 characterizes the values of the flows before the effect of carbonic acid gas (before carbonization).

State 2 characterizes the values of the flows after carbonization of the cement stone of the mortar.

The process of carbonization and the process of interaction of alkaline components of cement stone in mortar or concrete products with carbonic acid gas of atmospheric air begin from open surface.

On this basis, curves 1 in Fig. 2 which show the change in intensity of components of relative density of the carbonic acid gas flow before carbonization will reflect the value of effect of carbonic acid gas through open surface in initial moment of time. Fig. 2 shows that total density of a given flow significantly depends on relative pressure of water vapor in mortar  $\varphi$ . As  $\varphi$  increases, the value of density of carbonic acid gas flow decreases. This is due to the reduction of effusion component of total density of carbonic acid gas flow. The value of the total density changes from maximum at  $\varphi = 0.5$  to zero at  $\varphi = 0.99$ , while its diffusion component does not change significantly to the point  $\varphi = 0.9$ . The maximum value of effusion component of the flow density corresponds to the relative pressure of water vapor inside mortar  $= 0.5$ . In this case, the value is 3 times larger than diffusion component.

The components of density of gas flow (2) show the intensity of carbonic acid gas transported through spent layer of mortar after carbonization of cement stone to the front of reaction.

The total density of the flow transported through the unit of uncarbonized mortar surface is more than density of the flow transported through the unit of uncarbonized mortar, the ratio of the scalar values of the flows increasing from  $j_1/j_2 = 2.77$  at equilibrium pressure of water vapor inside mortar  $\varphi = 0.5$  to  $j_1/j_2 = 1.3$  at  $\varphi = 0.99$ . Here, the ratio of diffusion components of the flows ( $1.25 \div 1.3$ ) does not change significantly as  $\varphi$  increases in segment from  $\varphi = 0.5$  to  $\varphi = 0.99$ .

The equality of ratio of diffusion densities of the flows over the whole range of change in equilibrium pressure of water vapor  $\varphi$  inside mortar from  $\varphi = 0.5$  to the full saturation of capillaries with condensed moisture testifies that reduction in diffusion flow of carbonic acid gas after carbonization is caused by reduction in opening of microcapillaries due to the precipitation of insoluble products of reaction on their walls.

The parallel location of curves of the flows (about each other and about axis  $\varphi$ , see Fig. 2) which reflects the transfer of carbonic acid gas by diffusion both in uncarbonized and in carbonized layers of mortar testifies that scalar values of the flows do not depend on the relative pressure of vapor  $\varphi$  inside capillary body up to the full saturation, while effusion components of densities of the flow depend on  $\varphi$  both in uncarbonized and in carbonized layers of mortar and decrease from maximum at  $\varphi = 0.5$  to zero at  $\varphi = 0.99$ .

In this connection, to speak of diffusion restriction on increasing relative equilibrium moisture condition inside concrete of mortar [1, 2, 3] is to reflect physics of mass transfer not quite right. In this case, it is more correctly to speak of effusion restric-



tion on the transfer of carbonic acid gas to the front of reaction through spent layer of mortar or concrete after carbonization as relative equilibrium moisture condition inside capillary-porous body increases.

## Conclusions

1. It is suggested to differentiate porous space of concrete into microcapillaries with  $r \leq 1 \cdot 10^{-5}$  cm and into macrocapillaries with  $r > 1 \cdot 10^{-5}$  cm depending on the length of free path of air molecules ( $\ell \approx 1 \cdot 10^{-5}$  cm).
2. It is suggested for the first time to divide total flow of carbonic acid gas coming inside concrete from environment into diffusion and effusion components. Their quantitative correlations are determined analytically.
3. By the example of data on volumes of pores of cement/sand (1/2 mortar) the change in intensity of the flows (diffusion, effusion, and total) depending on moisture content in mortar is shown. It was demonstrated that the biggest intensity of carbonization is achieved at relative humidity of porous space of mortar  $\varphi=0.5$ , intensity of carbonization decreasing to zero if relative humidity of mortar goes to 1. In a large extent, relative humidity of porous space affects effusion component of gas flow density. Thus, in the case of changing relative humidity of porous space, it is effusion restriction of gas inflow that is true.

## References

1. **Алексеев, С. Н.** Коррозионная стойкость железобетонных конструкций в агрессивной промышленной среде / С. Н. Алексеев, Н. К. Розенталь. — М.: Стройиздат, 1976. — 205 с. = **Alekseev, S.N.,** Rozental, N.K. Corrosion resistance of reinforced concrete structures in corrosive industrial environment. Moscow: Stroyizdat, 1976, 205 pp.
2. **Долговечность железобетона в агрессивных средах: СССР-ЧССР-ФРГ** / С. Н. Алексеев [и др.]. — М.: Стройиздат, 1990. — 320 с. = **Alekseev, S.N.,** et al. Durability of reinforced concrete in corrosive mediums: USSR-ChSSR-Germany. Moscow: Stroyizdat, 1990, 320 pp.
3. **Франк-Каменецкий, Д. А.** Диффузия и теплопередача в химической кинетике / Д. А. Франк-Каменецкий. — М.: Наука, 1967. — 491 с. = **Frantz-Kamenetsky, D.A.** Diffusion and heat transfer in chemical kinetics. Moscow: Nauka, 1967, 491 pp.
4. **Лыков, А. В.** Теория сушки / А. В. Лыков. — М.: Энергия, 1968. — 472 с. = **Lykov, A.V.** Theory of drying. Moscow: Energiya, 1968, 472 pp.