

Changes in the topology of a concrete porous space in interactions with the external medium

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ABSTRACT

The article is devoted to some aspects of research of hostile environment influence on the concrete durability. The mechanism of formation of chaotically diversified difficult structure is described. Chemical interactions of cement with active components of diffusion in steam space are examined. Measures for receiving conditions under which the volume of products of reaction will be equal to the volume of the reacted alkaline components of a cement stone are offered. High-quality and quantitative changes in a pore space, which are irrespective of density and the relative molecular mass of reaction products are described. Besides, movement and distribution of gaseous products of reaction in volumes of a cement stone are simulated. Reasonable integrated dependences of influence of aggressive environment on various types of concrete surfaces are given. The methods of corrosion control offered in article allow substantially to lower or absolutely to exclude adverse effect of hostile environment on concrete and reinforced concrete structures already at a stage of selection of composition of concrete mix. In this case service life of concrete and reinforced concrete structures will increase.

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1. Introduction

Concrete and reinforced concrete, since the 2-nd half of the 20-th century, have been basic construction materials satisfying demands of building industries. Results of natural explorations and expert evaluations show that over 50% of all the building structures, depending on the designation of buildings and houses, are subjected to the process of carbonization in the atmospheric medium. The influence of aggressive media goes together with a decrease in the lifetime of these structures, and with

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losses arising from a stoppage of the production process for making repairs and reconstructions. In developed countries, the overall detriment due to corrosion of building constructions amounts to 4% of the national output and this detriment goes on increasing. The strength and durability of concrete in aggressive media are determined by the concrete structure which is formed in the process of cement hydration, the structure being of a capillary – porous character. Pores and capillaries having the dimension of 10^{-2} - 10^{-7} cm form a chaotically diversified complex system (Alekseev, 1993; Bazhenov, 2002). Chemical interactions of cement hydration products with active components of diffusing external media occur inside the porous space.

Meland (1985) experimentally showed that the action of gaseous carbon dioxide results in changes of reciprocal proportions in pores of different dimensions. The volume of pores larger than 5nm increases, whereas the volume of pores within the interval of 5-0.04 nm decreases (Neville, 1995). Carbonization changes the porous structure of hydrated cement pastes (Cebeci, 1986, Osheroov–Marshak, 2002). Since calcium hydrates contributes to formation of pores, the total porosity and volume concentration of large pores of the dimensions of 12.5-100 nm usually decrease (Dvorkin & Dvorkin 2007) and the interaction process of concrete with an external aggressive medium starts on the concrete surface. As the front of the reaction moves off the surface, the external medium transfer into the reaction zone takes place via a corroded layer of the concrete, the diffusion coefficient of which will be different from the diffusion coefficient of a non-corroded layer of concrete. However, while elaborating mathematical models, some researchers including the members of the European Bureau for Concretes (CEB) (e.g. Meier et al., 2007; Orchard et al., 1979), do not take into account this physical change and uphold all physical parameters entering the equation of diffusion that are characteristic of the state of a non-corroded concrete. But it does not correspond with reality. With an aim to bridge mathematical models and real processes of corrosion, the Mindess (2006) resort to a complication of these models by introducing additional integers in the equation of corrosion, which, to a greater degree, complicates obtainable solutions and, at the same time, does not reflect a real physical state of a corroded zone of concrete. One of the main objectives at this stage is development of effective methods on an exception of this kind of destructions. Processes occurring in concrete – aggressive medium interactions and possible ways of elongating the lifetime of reinforced concrete structures are discussed in the present article.

2. Theoretical framework

An original approach to solving the problem of capillary integral volume transformations and capillary differential distributions over their dimensions in chemical interactions of concrete with the external medium is suggested as a result of the present investigation. This approach is thought to define, more correctly, the physical state of a corroded zone of concrete in the equation of diffusion and to describe more correctly, from a physical viewpoint, the transportation of the external medium to a reaction zone.

Let us introduce a new notion “internal specific concrete surface reactive capacity” and designate it as L_S . This capacity is a ratio of volume density of products formed as a result of concrete reactions with the external aggressive medium L_V (kg/m^3) to the area of the porous space surface per unit of the volume, S (m^2/m^3), i.e.

$$L_S = \frac{L_V}{S} \quad (1)$$

The volume density of reaction products is determined by the expressions (Bazhenov, 2002; Wu, 2006):

$$L_V = C \times p \times f \times k, \quad (2)$$

where C is the cement consumption in concrete in kg/m^3 ; p is the relative content of cement stone alkaline components involved in the reaction with aggressive medium ions, in portions of the unit; f is the degree of completeness of the reaction of these interactions, in portions of the unit; k is the concrete reactive capacity which is the content of an active bound component of the aggressive medium, in portions of the cement mass. From Eq. (1) it is seen that the concrete specific surface capacity has a dimensionally of kg/m^3 and shows a mass of reaction produced products per unit of a porous space surface area.

2.1. The studied assumption

Suppose that the concrete is an isotropic material with respect to the concrete reactive capacity, i.e. value k is independent of the point position considered and is a feature of the structure of concrete as a quasi-homogeneous material. It is known that pores, in pore volumes per unit of a concrete volume and in their differential distributions over their dimensions in the volume unit, are quasi-homogeneously distributed in the concrete volume. The thickness of adsorption tightly-bound moisture on the inner surface of pores depends on a sort of the liquid adsorbed and on the kind of the sorbent, but it does not depend on capillary dimensions, if their diameter exceeds the doubled thickness of adsorbed moisture molecules and properties of liquid thin layers, as a sort of wedging pressure, are not decisive. In these conditions, the specific surface concrete reactive, capacity L_s will not depend on pore dimensions characterized by the radius. It will depend only on concrete reactive properties and the aggressive medium (Kosuhin et al., 2013; Krasovskii, 2013; Kurbatov et al., 2010; Lomachenko, 2014).

Thus, the mass of reaction products from the reaction between cement stone alkaline components and aggressive medium active components, per unit of the porous space surface area, will be the same for small capillaries and for large pores, i.e. the equalities are valid:

$$L_s(r_i) = \text{const}, \quad \frac{dL_s(r_i)}{dr_i} = 0.$$

At the known volume pore content V_n and inner surface area of all pores S per unit of the concrete volume, the pore hydraulic radius r_G will be equal to the ratio $r_G = \frac{V_n}{S}$. Knowing the hydraulic radius, one may find the inner surface area S_G of the unit of the pore length and the cross-section area A_G . They will be equal: $S_G = 2\pi r_G$; $A_G = \pi r_G^2$. Let us take into account that pore inner surfaces characterized by the dimension which is equal to the hydraulic radius r_G possess the same properties as physical pores of the radius r_i . On this basis, one may find the mass m_G (kg) of products formed in reactions of cement stone alkaline components with an active acid medium component in a unit-length pore with a dimension equal to the hydraulic radius r_G . This mass will be equal to:

$$m_G = L_s \times S_G \quad (3)$$

The mass, at the reaction product density which is equal to ρ_G , will take the volume in a unit-length pore:

$$V_G = \frac{m_G}{\rho_g} = \frac{L_s \times S_G}{\rho_G} \quad (4)$$

The mass of the cement reactive alkaline component, for example CaO , is determined, depending on the mass of produced products, from the equation of the interaction reaction with account for an equivalent ratio. For example, for the reaction of carbonization this equivalent ratio is equal to:

$$\frac{\text{CaO}}{\text{CaCO}_3} = \frac{56}{100} \quad (5)$$

With this account, the reacted CaO mass will be equal to: $m_{G,CaO} = m_G \frac{56}{100}$

2.2. Equivalent coefficient

At the known mass and density ρ_{CaO} , the volume of the reacted CaO with account for the equivalent ratio will be determined as: $V_{G,CaO} = \frac{m_{G,CaO}}{\rho_{CaO}}$.

The volume of accumulating products ΔV_G in a unit-length pore, with account for a loss of the volume taken by the reacted CaO in its equivalent ratio, is determined as the difference:

$$\Delta V_G = V_G - V_{G,CaO} = \frac{L_s \times S_G}{\rho_G} \left(1 - \frac{\rho_G}{\rho_{CaO}} \times \frac{56}{100} \right) \quad (6)$$

When accumulating, this volume will gradually fill the pore volume, starting from the pore wall and approaching the center. Designating the thickness of the accumulating products as δ_G , we may write the expression for the volume ΔV through δ_G and r_G on part of the pore length which is equal to the unit. This volume will be equal to:

$$\Delta V_G = \pi r_G^2 - \pi (r_G - \delta_G)^2. \quad (7)$$

Substituting (DELTA)VG and SG by their values, the equality above will take the form:

$$\delta_G = r_G - \sqrt{r_G^2 - B r_G}, \quad (8)$$

where

$$B = \frac{2L_s}{\rho_G} \left(1 - \frac{\rho_G}{\rho_{CaO}} \times \frac{56}{100} \right). \quad (9)$$

At $\delta_G = r_G$, the reaction products will fill in the volume of the pore of this radius. Substituting this value in Eq. (8), one may determine the radius at which capillaries and pores will be totally filled in by the reaction products:

$$r_{cr} = B = \frac{2L_s}{\rho_G} \left(1 - \frac{\rho_G}{\rho_{CaO}} \times \frac{56}{100} \right). \quad (10)$$

All the capillaries and pores, whose radius $r < r_{cr}$, will totally be filled in by the reaction products. On walls of the capillaries and pores, whose radius $r > r_{cr}$, there will deposit reaction products of the thickness δ_G . Let us re-write the expression in the brackets of Eq. (10) as

$$r_{cr} = \frac{2L_s}{\rho_G} \left(1 - \frac{\rho_G \times G_{CaO}}{\rho_{CaO} \times G_G} \right), \quad (11)$$

where G_{CaO} is the relative molecular mass of cement CaO which is in the equivalent ratio with the reaction products formed in cement stone interactions with the external medium active component; G_G is a relative molecular mass of the reaction products formed in the equivalent ratio with the cement CaO involved into the reaction.

3. Discussion of the Results

The analysis of Eq. (11) shows that when the expression in the brackets is equal to zero, the volume of reacted cement CaO will be equal to the volume of products formed in the reaction. If the reaction products are insoluble or little soluble, then they take, in the equivalent ratio, a free volume previously taken by CaO. There should be no changes in a general picture of pore and capillary locations, either in the porous space integral volume or in the differential distribution of pores over dimensions (Novichkov, 2001). When the relative molecular mass of reaction products G_G exceeds the relative molecular mass of G_{CaO} at relative equalities of their densities, i.e. at $\rho_G = \rho_{CaO}$, the denominator in Eq.

(11) in the brackets will be larger than the numerator. This is the evidence that the reaction product volume exceeds the reacted CaO volume taken by CaO before the reaction in their equivalent ratio. When insoluble or little soluble, the reaction products will be accumulating in pores and in concrete capillaries, filling in capillaries of a small radius and producing a layer of insoluble compositions of thickness (δ) on the walls of capillaries and pores of large dimensions (Sagneva et al., 2012). Here at both integral volume of pores and differential picture of pore distributions over dimensions will change. The larger is the difference in the expression $(\rho_{CaO} \times G_G - \rho_G \times G_{CaO})$, the larger is the difference between volumes of reaction products and volume of reacted CaO in their equivalent ratio.

3.1. Statement of facts

Therefore, a larger volume of pores will be taken by reaction products accumulating on their walls. If the volume of reaction products exceeds a permissible limit for this sort of concrete, then a pressure will appear on pore walls in the process of reaction product crystallization out of the mortar. When the value of stretching deformations in a cement stone around the pores due to this pressure exceeds the limit, there will appear, first, micro-cracks in the cement stone. Later, such cracks merge with the formation of entire cracks, resulting, finally, in scales of the worked-out part of the concrete cross-section. This argumentation is confirmed by the experimental investigations of carbonization (Solomatov & Tahir, 1989; Stol'nikov, 1953; Wu, 2006; Ramachandran et al., 1981). If the inequality $\rho_G \times G_{CaO} > \rho_{CaO} \times G_G$, is fulfilled, the relative molecular mass of the reaction products GG will be less than the molecular mass of the cement CaO.

At a relative equality of their densities $\rho_G = \rho_{CaO}$, the volume of reaction products will be less than the volume taken by CaO before the reaction, in their equivalent ratio. In the case of insolubility or little solubility of the reaction products, there will take place the softening of the cement stone with an increase in the integral volume of a porous space and with a displacement of the pore distribution curve apex of pore differential distributions over their dimensions in the direction of an increase in the dimension of a pore average statistical radius (Dobrolyubov et al., 1983). The softening of the concrete cement stone may occur not only due to a decrease in the volume taken by the reaction products with respect to the volume of the reacted cement CaO in their equivalent ratio, but also due to the formation of reaction products soluble in liquid or gas and the formation of solutions or gaseous mixtures. In this case, the density ρ_G of liquid or gaseous reaction products will be less than the density of ρ_{CaO} as a solid body, i.e. the inequality $\rho_G < \rho_{CaO}$ is observed. At the equivalent equality of the reaction products and the reacted CaO, (i.e. if the equality $G_G = G_{CaO}$ is observed), then the expression in the brackets of Eq. (11) will take the form

$$r_{cr} = 2L_S \left(\frac{1}{\rho_G} - \frac{1}{\rho_{CaO}} \right). \quad (12)$$

As seen from Eq. (12), the greater is the difference in the expression $\rho_{CaO} - \rho_G$, the greater is the softening which will result in an increase of the integral porous volume and an increase in the pore hydraulic radius. If a relative molecular mass of gaseous products of the reaction is larger than a relative molecular mass of the reacted CaO in their equivalent ratio, then the inequality $\rho_{CaO} \times G_G > \rho_{CaO} \times G_{CaO}$ is observed. This is the evidence that the volume of the liquid or gaseous reaction products will be larger than the volume of cement stone components. If the difference in these volumes exceeds the porous volume in which the exchange reaction has taken place, the liquid reaction products will flow off the concrete body as mucus. The migration of gaseous reaction products will take place independently of the difference in volumes of the reaction and cement stone components in their equivalent ratio, according to the mass transfer law, either by diffusion or by effusion.

Qualitative and quantitative changes in a porous space, independently of the density and relative molecular mass of the reaction products, will be determined to a great extent by the specific surface concrete reactive capacity LS . With an increase in LS , volume of the reaction products will increase, which, in case of insolubility or weak solubility of reaction products, will lead to a decrease in the porous space integral volume and to a shift of the curve apex of the differential expansion of pore dimensions in the direction of a decrease in the pore radius (Furmanov, 2009; Ureckaya & Batyanowski, 2001; Valsov, 1998; Liang & Lin, 2003; Papadakis & Efstathion, 2006).

4. Conclusions

For the first time the analytical expression for a critical dimension of a capillary radius r_{cr} for a cement stone of concretes affected by an aggressive external medium has been obtained. The capillary radius r_{cr} dependence on the integral specific concrete surface reactive capacity LS was discovered. All capillaries of the radius $r < r_{cr}$ will be filled in by products of the reaction between a diffusing external aggressive medium and reactive components of a cement stone. If the reaction products are insoluble or little soluble, they will create, when accumulating, a pressure on walls of capillaries of given dimensions and will destroy the concrete integrity in the forms of cracks and scales in the concrete.

In known conditions of exploitation characterized by a chemical composition of the external medium, one can avoid the above-mentioned damage as early as at the stage of selecting concrete compositions by regulating the value of the internal specific concrete surface reactive capacity LS . This can be made by the introduction into the concrete of a mixture of special chemical additives contributing to a decrease of a relative molecular mass of reaction products in comparison with a relative molecular mass of reacted alkaline components of the cement stone. In this case, it is desirable to obtain the conditions that the volume of the reaction products be equal to the volume of the reacted alkaline components of the cement stone or should exceed it insignificantly. In this case, the density of the concrete in the process of its exploitation will increase with no damage in its structure, thus making a barrier to the diffusion of the external medium enhancing the lifetime of concrete and reinforced concrete frames.

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