Process of Concrete Carbonation Under Aggressive Carbon Dioxide Attack

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ABSTRACT

It is proved, that in a wide range of concrete saturation (which means degree of pores filling with water) the principal factors controlling corrosion (carbonation) of concrete are the processes proceeding in a gaseous and liquid phases; the formulas recommended for engineering calculations are presented. For the approximate analysis the humidity, temperature and concentration of an aggressive component could be considered as constant. The basic purpose of the given research is the calculation of speeds of movement and depth of front of corrosion (carbonation), that enables to predict service life of the structure.

INTRODUCTION

In a basis of the given work the principle of division of complex process into elementary components with their subsequent mathematical description is laid in such a manner that a more complicated kind of corrosion covers the simpler ones; and with certain simplifications of the equations both having certain physical sense, the transition from a complex model to a simpler one takes place.

The application of such approach allows us to examine corrosion of concrete and reinforced-concrete structures as a single process, irrespective of a type of corrosion. This procedure has certain advantages. It is methodically single (formalized logic, a single set of constants, etc.),and in the practical sense (a single technique of making experiments, a single algorithm of a numerical solution of   the problem).

DISCUSSION OF RESULTS OBTAINED

The usually used formula for practical calculation of carbonation front movement velocity assumes that the speed of processes of carbonation is controlled and limited by the speed of diffusion of gas in concrete pore space. However, this assumption requires essential verification. First, the coefficient of diffusion D of gases is higher by a few orders, than coefficient of diffusion of ions in solutions. For gases: $D \sim 10^{-1}$ cm^2/sec, for ions in a solution $D \sim 10^{-5} ... 10^{-6}$ cm^2/sec. Secondly, the concentration of aggressive gas is much lower than volumetric concentration of ions in a solution. According to Thomson-Kelvin, between the radius of curvature of a liquid drop and a relative pressure of steam above the meniscus the certain relation exists, which is expressed by the formula:

$$\ln a = \frac{2Vm\sigma}{Rtr} = \frac{\varphi\delta_0}{kTr} \tag{1}$$

$a = \dfrac{p}{p_0}$ - relative pressure of steam above meniscus;

V_M - molar volume of a liquid;

σ_0 - superficial tension;

R - universal gas constant;

T - absolute temperature;

R -radius of meniscus ;

$\varphi = 2\sigma\delta_0{}^2$ - conditional energy of connection between two molecules;

δ_0 - intermolecular distance;

K - Boltsman's coefficient.

The specific radius of capillaries r_k corresponds to specific humidity. All pores, for which $r<r_k$, will be filled with a liquid as a result of steam condensation, and all pores, for which $r>r_k$, will be dry. From the above it follows, that at $a = 60\%$ the filling of pores with the liquid reaches such a degree, which practically excludes carbonation in gas phase ($a = 60\%$, $r \approx 10^{-9}$ m), that proved to be true other researchers. It is known, that intensive carbonation of heavyweight concrete is observed at humidity of 50-80 %. With increase of humidity the carbonation is slowed down it is related both to a rather high amount of pores condensing moisture and to the delayed speed of removal of water from the dense concrete.

The physical and chemical processes of corrosion of concrete in gas environment within the framework of the developed model can be presented as follows:

Physical process or chemical reaction	Equation of chemical reaction	Type of differential equation of the process
1 Carbon dioxide diffusion in pore space of concrete (C_A)		Differential equation of diffusion removal
2. Gas sorption in pore liquid (C_B)		Differential equation of sorption of first order
3. Reaction of formation of carbonic acid $CO_2+H_2O=H_2CO_3$	K_1 $C_B \rightarrow C_D$	Kinetic equation of homogeneous chemical reaction
4. Dissolution of calcium hydroxide in a liquid phase	β_p $m \rightarrow C_E$	Differential equation of first order
5. Mass transport of calcium hydroxide in a liquid phase		Differential equation of first order
6. Reaction of formation of calcium carbonate $H_2CO_3+Ca(OH)_2 = CaCO_3+2H_2O$; $CO_2+Ca(OH)_2= CaCO_3+H_2O$	K_3 $C_B + C_E \rightarrow C_G$	Kinetic equation of homogeneous chemical reaction of first order
7. Formation of sediment of $CaCO_3$	β_H $C_G \rightarrow g$	Differential equation of first order

In the given model the equations of physical and chemical processes of carbon acid corrosion of concrete in gas environments are formulated without simplifications of basic character, taking into account the fact that nonequilibrium and non-stationary character determines the kinetics of processes of corrosion. Proceeding from the above it is evident, that the speed of processes of corrosion in gas environments is controlled by humidity of surrounding air, i.e. the degree of filling pores with the liquid.

Specified above allows to make a conclusion, that in some cases the process of corrosion can be governed by processes proceeding in a liquid phase, but in others – in a gaseous one.

The area, where limiting are the processes proceeding in a liquid phase, is characterized by inequality, which can be presented with allowable for practical purposes accuracy as:

$$\sqrt{\frac{D_g}{D_0}} \cdot \frac{C_g}{C_0} \leq \frac{W}{1-W} \tag{2}$$

D_g - is the diffusion coefficient of carbon dioxide in gaseous environment;
D_0 - diffusion coefficient of carbon dioxide gas in water;
C_g - concentration of carbon dioxide in water;
C_o - concentration of carbon dioxide in gaseous environment;
W - degree of filling pores with water.

Assume that:
$D_g \approx 10^{-1}$ cm^2/sec, $D_0 \approx 10^{-5}$ cm^2/sec, $C_g \approx (0{,}6\text{-}2{,}0) \cdot 10^{-3}$ g/l
$C_o \approx (0{,}01\text{-}0{,}025)$ g/l then $W \geq 0{,}8$, that corresponds to relative humidity of air $\varphi > 0{,}95$. It should be noted, that the Thomson-Kelvin's formula (1) produces a somewhat result. It is explained by the following: the formula assumes, that the liquid phase, should moisten the walls of capillaries. If wetting is incomplete, or the walls of capillaries are hydrophobic, then the spontaneous condensation could be absent. This circumstance is extremely important, because it specifies one of the most probable ways of protection against gas corrosion.

On the basis of the auto modeling solution developed before (2), the formula for engineering computations could be derived.

$$\alpha_{lq} = \sqrt{\frac{2D_{lq}C_{lq}\varepsilon_p W}{m_0}}, \ W < 0{,}8 \ (\varphi < 0{,}95) \tag{3}$$

ε_p - effective porosity;
C_{lq} - concentration of an aggressive component in a liquid phase;
D_{lq} - molecular coefficient of diffusion in liquid environment.

When diffusion processes a gaseous media are dominant, the speed of carbonation process is equal to:

$$\alpha_{lq} = \sqrt{\frac{2D_g C_g \varepsilon_p (1-w)}{m_0}}, \ \text{where } w > 0{,}8 \ (\varphi > 0{,}95) \tag{4}$$

Comparing the formula (4) with the one known earlier, it is clear, that the results of calculations with their use, differ from other by a multiplier (1-W) which reflects the fact, that at W>0,8 limiting are the processes of transfer in the space which has not been filled with a liquid phase, and at W=l the speed of corrosion is equal to zero, that the previous formula does not take into account.

For performance of numerical computation by the formulas (3) and (4) it is convenient to present in the from:

$$\theta_{lq} = \frac{a_{lq}}{\sqrt{D_{lq}\,\varepsilon_p}} = \sqrt{\frac{2C_{lq}W}{m_0}} \ , \ W < 0{,}8 \ (\varphi<0{,}95) \tag{5}$$

$$\theta_{g} = \frac{a_{g}}{\sqrt{D_{g}\,\varepsilon_p}} = \sqrt{\frac{2C_{g}(1-W)}{m_0}} \ , \ W > 0{,}8 \ (\varphi>0{,}95) \tag{6}$$

Where θ_{lq}, θ_{g} - is reduced speed of carbonation.

The value of ($\sqrt{D_{g}\varepsilon_{II}}$) is nothing other than effective coefficient of diffusion D_{eff}. On the basis of the above and also on the basis of experimental data, the dependence of speed of movement of carbonation from on the degree of pores, filling with liquid is of the form (fig.1).

In the area of existence of the solution (5) the speed of corrosion is limited by mass transport processes in liquid, and in area (6) – in a gaseous phase, i.e., the process of diffusion of gases is a limiting one at a high degree of filling pores with a liquid phase.

In figure 2 the example of numerical calculation θ (W) for the concrete with a reactivity of 50, C_{CO_2}=10 % is given at 20°C. From two meanings calculated according to the formulas (4) and (5), the least is chosen, which is the characteristic of carbonation process, as the speed of carbonation depends upon D_{eff} – a quantitative characteristic of the way of delivery of an aggressive component.

The formulas (2 and 3) qualitatively correctly illustrate the dependence of coefficient of carbonation speed on the degree of filling pores with water. Quite important is the fact, that in most cases of carbonation, examined in practice, limiting are the processes of transport occurring in a liquid phase, that requires reconsideration of the existing technique of calculation of carbonation speed.

Experimental data and the data of field studies show, that the standard requirements for concrete and reinforced-concrete structures are overestimated. The results of researches presented in this paper, allow us to solve this problem.

First, the question concerning the determination of effective coefficient of diffusion still remains to be solved. Different sources determine its value differently, that makes comparison of experimental data impossible Second, the classical formula of calculation of effective

coefficient of diffusion does not take into a recount real mechanisms of an aggressive component transport, that results in errors in calculations.

CONCLUSIONS

It may be concluded that one of major factors influencing carbonation (corrosion) processes, is the degree of filling pores with water. Thus, the calculation of corrosion resistance of concrete and reinforced-concrete structures is reduced to such concrete mix design, that secures a degree of filling pores with water which will not exceed a specified level.

This value is dependent upon specific air humidity of the area, where the construction will take place, upon certain porosity and reactivity of concrete and that is a quite soluble task.

The character of dependence of a degree of filling pores with water on the above parameters can be found experimentally, having received semi-empirical relations similar to the Rode formula in soil science [3], or more exact analytical dependence's can be found.

REFERENCES
GousevB.V., Faivousovich A.S., Stepanova V.F., Rozentahl N.K. Mathematical models of processes of concrete corrosion M., "TIMR", 1996.
Moskvin V.M., Ivanov F.M., Alexeev S.N., Gouzeev E.A. Corrosion of concrete and reinforced concrete, methods of their protection. M., Stroiizdat., 1980, pp 536.
Polak A.F, Ratinov K. B., Gelfan G.N. Corrosion of reinforced concrete structures of petrochemical buildings. M., Stroiizdat., 1971,ppl76.
Polak A.F., Modeling of corrosion of reinforced concrete structures and forecasting of their durability. Results of science and engineering. Corrosion and protection against corrosion. M.,VINITI, 1986, v. 12.
Polak A.F., The essentials of corrosion of reinforced concrete and mathematical modeling with application of computers Ufa, UNI, 1986.
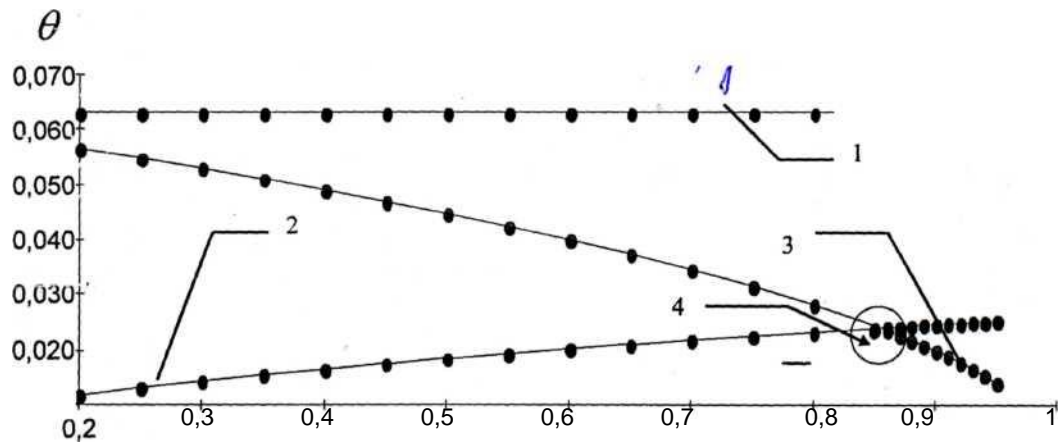
Fig.2. Relationship between reduced coefficient of carbonation speed and the degree of filling pores with water.
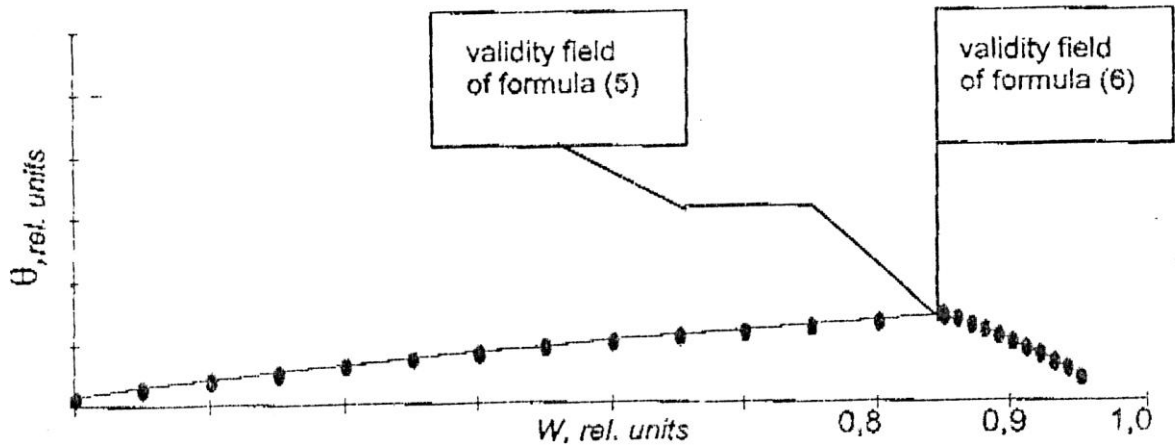

Fig.1. The dependence of speed of movement of carbonation front θ on the degree of pores' filling with liquid W:

1- according to formula (1): calculation using D coefficient relative humidity 75%;

2- liquid phase formula (2) ;

3- gaseous phase formula (3);

4- Intersection region of solution (2) and (3).