Pergamon

Cement and Concrete Research, Vol. 26, No. 3, pp. 475-490, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00003-8

CORROSION OF HARDENED CEMENT PASTE BY ACETIC AND NITRIC ACIDS PART III: INFLUENCE OF WATER/CEMENT RATIO

V. Pavlík
Department of Material Engineering,
Faculty of Civil Engineering, Slovak Technical University,
Radlinského 11, 813 68 Bratislava, Slovakia

(Refereed)
(Received March 23, 1995; final form November 30, 1995)

ABSTRACT

The influence of water/cement ratio as a factor controlling the rate of corrosion of hydrated cement paste (HCP) in solutions of acids was investigated. The rate of corrosion decreases with increase in cement content per unit volume of HCP (a decrease in water/cement ratio). There are two main causes accounting for this fact. One is the increased neutralization capacity of HCP's with an increased cement content, the other is the increase in diffusion resistance of layers of corrosive products of HCP. The first of the two effects is supposed to be more important. Finally mathematical relations were found, to express the depth of HCP corrosion as a function of the water/cement ratio, the concentration of the aggressive acid solution, and the duration of attack.

1. Introduction

Hardened cement paste (HCP) is severely attacked by solutions of acids. In the course of an acid attack a layer of corrosive products develops on the surface of HCP. Properties of the layer, such as porosity and bulk density, depend on the type of attacking acid, concentration and pH value of acid solution, composition of cement and other factors. In the case where the HCP is attacked by an acid producing easily soluble Ca-salt, the corroded layer consist mainly of hydrated SiO_2 and, depending on pH value of the solution, also Al_2O_3 and Fe_2O_3 hydrates. Changes in chemical composition of corroded HCP's specimens are described in more detail, and supported by adequate quotations in part I. and part II. of this article [1,12]. The bulk density of the dried layer of corrosive products is extremely low and porosity extremely high [2–7]. The lowest values of bulk density (of the completely or nearly completely corroded HCP's with w/c of 0.4) were reported to be about 410 kg/m^3 [3–6]; the author of this article even found values below 400 kg/m^3. The values varied depending on composition of test specimens and conditions of the tests. Specimens, having the lowest bulk densities, had the maximum values of total porosity—exceeding 80% [3–7]. The porous mass of the layer of corrosive products acts as a protective barrier against the direct contact of the uncorroded cement paste with the acid solution. During the corrosion process the aggressive substance is transported through this barrier almost entirely by diffusion. The degree of corrosion in this case depends on $\sqrt{t}$,, where t is the time of exposure.

Water/cement is one of a number of factors that control the rate of corrosion of HCP's in solutions of acids. Increase in w/c results in an increase in rate of corrosion [2–8]. This effect is explained by reduction in permeability of the layer of corrosive products. Changes in uncorroded HCP's permeability are not sought to have effect on the process [8]. The influence of w/c , however, is reported as relatively small [2–8,11].

To assess the extent of corrosion over long periods of time, mathematical models have been developed that express the extent of HCP corrosion as a function of one or more of the above mentioned corrosion controlling factors. The equations published so far were divided into two groups: (a) those, obtained by regression analysis from experimental results (empirical equations) and, (b) those, developed by theoretical analysis of the corrosion process (theoretical equations).

Empirical Equations. Most of the empirical equations already published express the extent of HCP's corrosion as a function of two factors: the concentration of aggressive acid (c) and the time of exposure of the specimens in an aggressive solution (t). These equations are usually written in a general form as follows [3,6,12]:

$$d = k.c^{m}.t^{n} \tag{1}$$

where: d - is depth of HCP corrosion, or thickness of the corroded layer;

k -empirically determined coefficient which depends mainly on type of aggressive acid, chemical composition of the cement, water/cement of HCP and conditions of test;

m, n - empirically determined exponents, with values ranging usually from 0.5 to 0.7.

Theoretical Equations. To describe corrosion of concrete in carbonic acid, Grube and Rechenberg [9,10] developed a model, theoretically based on Fick's laws of diffusion, as follows:

$$d = \sqrt{\frac{2.D.A_L}{m_L.A_{ges}}(c^{*}_{s} - c_L)} \cdot \sqrt{t} \tag{2}$$

where: d - is thickness of destroyed concrete layer in cm ,

D - $Ca(HCO_3)_2$ diffusion coefficient in cm^2/s of the protective (gel) layer,

m_L - mass of soluble matter in g of CaO per cm^3 of concrete,

c^{*}_{s}- $Ca(HCO_3)_2$ concentration in g/cm^3 in the solution surrounding intact concrete,

c_L-$Ca(HCO_3)_2$ concentration in g/cm^3 in the solution which is unaffected by the concrete,

A_L/A_{ges}-ratio of soluble matter area to total area,

V_L/V_{ges}-ratio of the volume of soluble constituents (volume of hardened cement paste— if insoluble aggregate is used) to total volume, $[A_L/A_{ges} = V_L/V_{ges}]$

The object of this paper is to evaluate the water/cement ratio as a factor, influencing the rate of HCP corrosion, and express this mathematically. Only attacks of acids, such as nitric, acetic and other acids producing the easily soluble calcium salts, will be taken into consideration.

2. Preliminary Analysis of the Problem

2.1 Equation by H. Grube and W. Rechenberg [9,10]. Let us look closer at the equation (2). The mass of soluble matter in g of CaO per cm^3 of concrete (m_L) by our opinion can be expressed as follows:

$$m_L = \frac{m_c \cdot \alpha}{V_{ges}} \tag{3}$$

In equation (3) we used two new symbols: m_c - denoting the mass of cement, and α - denoting the mass fraction of soluble matter (CaO) in the cement.

The relationship between the three variables m_L, A_L and A_{ges} in the equation (2), can be also written as follows, when we use equation (3):

$$\frac{A_L}{m_L \cdot A_{ges}} = \frac{V_L}{m_L \cdot V_{ges}} = \frac{1}{\dfrac{m_c \cdot \alpha}{V_L}} \tag{4}$$

where: $\dfrac{m_c \cdot \alpha}{V_L}$ - denotes the mass of soluble matter in g of CaO per cm^3 of HCP.

Equation (2) can also therefore be written in the following form:

$$d = (2 . D)^{0.5} . \left(\frac{V_L}{m_c \cdot \alpha} \right)^{0.5} . (c_s^* - c_L)^{0.5} . (t)^{0.5} \tag{5}$$

Equation (5) defines the influence of the cement content per unit volume of HCP, as well as the influence of other factors, on the corrosion of concrete. (Equations (4) and (5) further show, that depth of corrosion of concrete in acids does not depend on the aggregate content, or, they do not evaluate the influence of this factor. The most important role the aggregate particles play in the cement composites corrosion is probably the prolongation of the diffusion trajectory of the aggressive substance round the aggregate grains. This factor, which Romben [7] terms the "labyrinth effect", will be solved in an article to be published in the future.

2.2 Modification of Empirical Equations. Addition of a Supplementary Factor—The Water/ Cement Ratio.

Calculation of cement content per unit volume of cement paste and its influence on corrosion rate. The mass of cement per unit volume of HCP is given by the water/cement ratio of the paste. When the cement paste sets, it acquires a relatively stable volume (V) that is approximately equal to the volume of cement (V_c) plus the volume of water (V_w); entrapped air and volume changes are neglected;

$$V = V_c + V_w \tag{6}$$

In this paper two different types of symbols and units are used. The ones in eqs. (2)–(5) are quoted from the papers by Grube and Rechenberg [9,10]; the present ones are used in other paragraphs in this paper.

Volumes of cement (V_c) and water (V_w) in the cement paste can be calculated using the density of cement and water, and the water/cement ratio of the cement paste (w/c). Since the w/c is generally given by mass, it can be written as follows:

$$w/c = \frac{m_w}{m_c} \tag{7}$$

where: m_w - is mass of water, and m_c - is mass of cement.

The approximate value of the volume of an HCP then can be calculated, using the density of cement and water, and eqs. (6) and (7) as follows:

$$V = \frac{m_c}{\rho_c} + \frac{m_c . w/c}{\rho_w} = m_c . \left(\frac{1}{\rho_c} + \frac{w/c}{\rho_w} \right) \tag{8}$$

where: m_c - is mass of cement, V - is volume of HCP, w/c - is water/cement of the cement paste, ρ_c - is density of cement, and ρ_w - is density of water.

Finally the approximate value of the cement content per unit volume of HCP ($m_{c,u,w/c}$) can be calculated with use of eq. (9).

(Subscripts ($_{c,u,w/c}$) stand for cement, unit volume, and actual value of w/c.)

$$m_{c,u,w/c} = \frac{m_c}{V} = \frac{m_c}{m_c\left(\frac{1}{\rho_c} + \frac{w/c}{\rho_w} \right)} = \frac{1}{\frac{1}{\rho_c} + \frac{w/c}{\rho_w}} = \frac{\rho_c \cdot \rho_w}{\rho_w + \rho_c \cdot w/c} \tag{9}$$

Influence of water/cement ratio of HCP on the rate of corrosion. The rate of corrosion of HCP's in solutions of acids decreases with the cement content per unit volume of HCP. To decompose the unit volume of an HCP containing a z-times higher amount of cement than the unit volume of an HCP of a referent specimen, requires, under the same conditions, a z-times higher amount of the aggressive substance (the paste has a z-fold neutralization capacity [4]). Chemical reactions taking place in the corrosion zone produce, at the same time a z-fold amount of soluble corrosive products. In our experiments the HCP test specimens with a w/c = 0.4 were taken as the referent ones. "z", therefore, was defined as the quotient of the cement content per unit volume of HCP being under study and the cement content per unit volume of the referent specimen with w/c = 0.4:

$$z = \frac{m_{c,u,w/c}}{m_{c,u,0.4}} = \frac{\dfrac{\rho_v \rho_c}{\rho_c . w/c + \rho_v}}{\dfrac{\rho_v \cdot \rho_c}{\rho_c \cdot 0.4 + \rho_v}} = \frac{\rho_c \cdot 0.4 + \rho_v}{\rho_c . w/c + \rho_v} = \frac{1}{B . w/c + A} \tag{10}$$

where: $m_{c,u,w/c}$ - is the cement content per unit volume of the HCP with water/cement ratio w/c,
$m_{c,u,0.4}$ - is the cement content per unit volume of the HCP with w/c = 0.4 (referent specimen),
A, B - are coefficients defined by the expressions (11) and (12):

$$A = \frac{\rho_v}{\rho_c \cdot 0.4 + \rho_v} \tag{11}$$

$$B = \frac{\rho_c}{\rho_c \cdot 0.4 + \rho_v} \tag{12}$$

It may be claimed, that the rate of HCP corrosion in an acid solution at any given moment of time is proportional to the rate, at which the aggressive substance, being transported through the layer of the corrosion products by diffusion, enters the reaction zone. The diffusion flow of the aggressive substance through the unit area of a cross-section of the layer of corrosive products depends on the concentration gradient of the aggressive substance at the cross-section and on the resistance of this layer to diffusion.

In the next paragraphs we will compare the diffusion flows of the aggressive substance through two, equally thick, layers of corrosive products of HCP's with different w/c's. At equal thickness of these layers, and at equal concentrations of the aggressive substance on the outer, and the inner sides of these layers (c_0 - in the aggressive solution, and c_1 - at the pH-neutral point in the zone of corrosion [12]), the difference between the diffusion flows of the aggressive substance through each layer depends, in our opinion, mainly on the differences of diffusion coefficients (D_1) and (D_2) in each layer. Under presumption that the difference between the diffusion coefficients is small or negligible, the diffusion flows of the aggressive substance through each layer would be nearly equal. This presumption can be supported by data published by Bajza [2,3] and Bajza and Rouseková [4]. According to these authors the total porosity of HCP's with w/c's of 0.1, 0.3 and 0.4, after 1488 days storage in water, were 14.4%, 27.1% and 34.4%, respectively [3]. Total porosities of specimens stored in acid solutions were considerably higher. At 1460 days in a solution of 3% acetic acid and in a solution of 3% formic acid, the total porosities of the completely or almost completely corroded specimen were 66.1%, 78.3% and 80.2%, and 74.3%, and 79.5% and 81.9%, respectively. These data point to the fact that even when w/c strongly affects values of the total porosity of HCP's stored in water, it has only a slight effect on the total porosity values of the corroded specimens. The small differences between these enormous values of the total porosities of the corroded specimens corresponds with our hypothesis about the small difference in diffusion resistance of the corroded layers. Due to the lack of accurate data on a diffusion resistance (of the corrosive layers of HCP's with different w/c's) we will ignore the differences and consider the diffusion coefficients and, consequently, also the diffusion flows of the aggressive substance through the different layers of corrosive products as equal.

To decompose an infinitesimally thin segment of HCP with a cement content per unit volume a z-times higher than in the HCP with w/c = 0.4, a z-fold amount of the aggressive substance is required. Transport of a z-fold amount of the aggressive substance through the corroded layer, will take, under the same conditions, a z-fold longer interval of time. If decomposition of each infinitesimally thin segment of HCP takes a z-fold longer interval of time, decomposition of the entire specimen, or part of it, will then also take a z-fold longer interval of time.

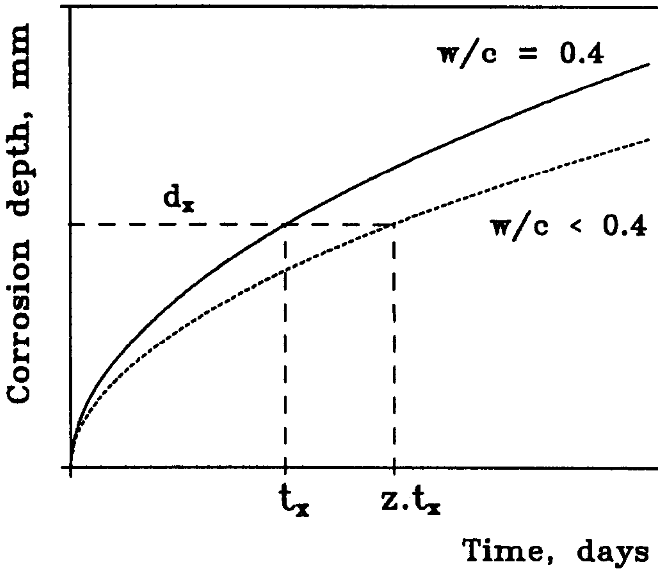

FIG. 1.
Comparison of exposure times of HCP's with different values of w/c, required to obtain the same depth of corrosion.

Empirical equations developed by the author [12] to calculate depth of corrosion of the HCP with w/c = 0.4 have a general form (13):

$$d = K_{0.4} . c^{m} . t^{n} \tag{13}$$

where: d - is depth of corrosion,

$K_{0.4}$ - is coefficient characterizing the corrosion process of HCP with w/c = 0.4 in a given aggressive solution,

c, t - is concentration of the aggressive solution and time of its action,

m, n - are empirical exponents.

Analogous equation (14) would also be valid, in our opinion, for an HCP with any other (but not too extreme) value of w/c:

$$d = K_{w/c} . c^{m} . t^{n} \tag{14}$$

where: $K_{w/c}$ - is coefficient characterizing the corrosion process of HCP with any actual value of w/c in a given aggressive solution, and

m, n - are exponents identical with those in equation (13).

HCP's with different values of w/c will undergo the same depth of corrosion in various time intervals. To be corroded to a certain depth (d), the process of corrosion of an HCP with water/cement ratio w/c will take a z-times longer (shorter) interval of time, compared with the same process of an HCP with w/c = 0.4 of the referent specimen (Figure 1); "z" is defined by eq. (10). At an equal depth of corrosion (d) we will get, from eqs. (13) and (14), equation (15):

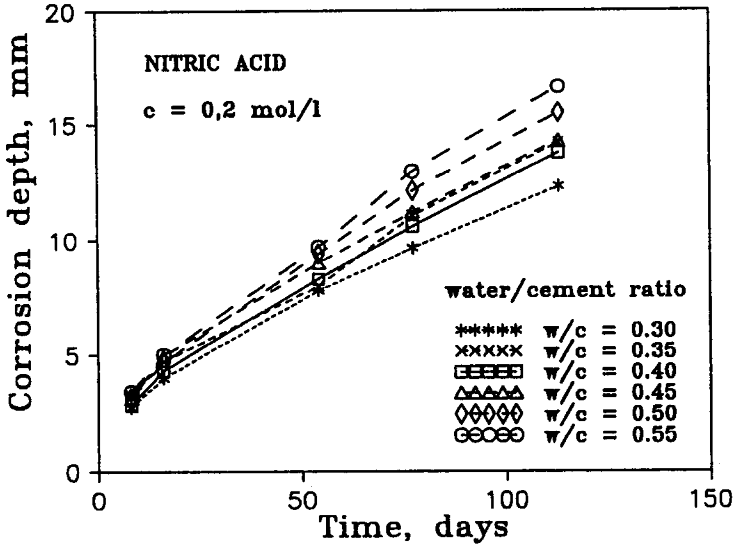

FIG. 2.

Depth of corrosion of HCP's with different w/c's related to the duration of the acetic acid solution (experiment I).

$$K_{0.4} \cdot c^{m} . t^{n} = K_{w/c} \cdot c^{m} . (z . t)^{n} \qquad (15)$$

From that:

$$K_{w/c} = \frac{K_{0.4}}{z^{n}} \qquad (16)$$

Substituting eq. (16) into eq. (14) we will get eq. (17). Depth of corrosion of HCPs with any value of w/c then can be calculated as follows:

$$d = \frac{K_{0.4}}{z^{n}} . c^{m} . t^{n} = K_{0.4} \cdot \left(\frac{t}{z} \right)^{n} \qquad (17)$$

Equation (17) would be valid only under the same conditions as those of the experiment leading to empirical equation (13). Substituting z from eq. (10) into eq. (17) we obtain the final equation (18):

$$d = K_{0.4} \cdot (A + B . w/c)^{n} . c^{m} . t^{n} = K_{0.4} . W^{n} . c^{m} . t^{n} \qquad (18)$$

Factor "W = A + B.w/c" extends or modifies the basic empirical equation (13) by incorporating into it the influence of water/cement ratio. Comparison of eq. (18) with eq. (5) shows consistency of both.

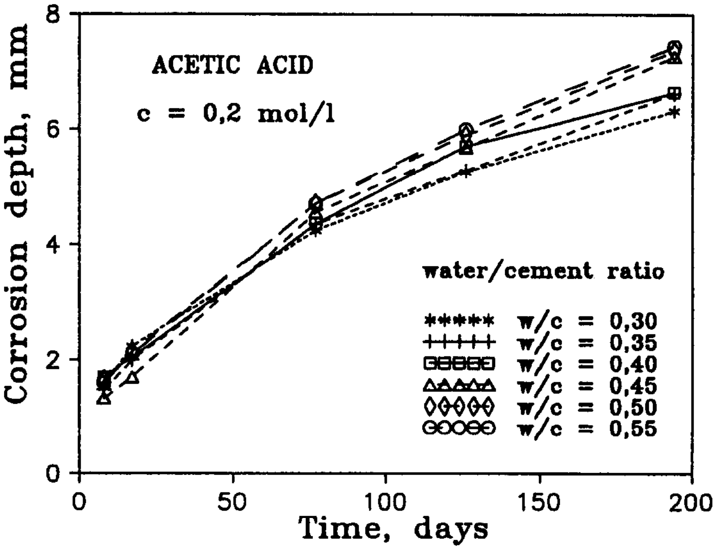

FIG. 3.
Depth of corrosion of HCP's with different w/c's related to the duration of the acetic acid solution attack.

3. Specimens and Test Procedure

Test specimen were prepared using glass tubes filled with cement paste from portland cement and water. The tubes were only open at one end. Water/cement of the cement pastes ranged from 0.3 to 0.6. Density of the cement was 3100 kg/m^3. The specimens were left to harden for 28 days in water and then were placed in solution of acetic acid or nitric acid. Concentration of each acid solution was kept at 0.2 mol/l. Both acids produce easily soluble Ca-salts, therefore, the layer of corrosive products on the surface of the HCP's was porous and permeable. During the experiments the depth of HCP's corrosion was measured regularly. The depth of corrosion was defined as the distance between the end of a glass tube (the surface of the specimen before corrosion) and the boundary between corroded and uncorroded HCP—which was visually clearly distinguishable. The distance was measured using calipers. The experiment have also been described in part I of this paper [1]. Results of attack of nitric acid are from two separate experiments.

4. Test Results and Their Evaluation

Figs. 2–5 show the increase in depth of corrosion of HCP's with different w/c in solutions of nitric and acetic acids related to time. The aggressive effect of nitric acid is greater than that of acetic acid. The aggressive effects of both acids, shown in Figs. 2 and 3, are compared in Fig. 4. Curves in Fig. 4 are graphs of equations found by regression analysis (Table 1).

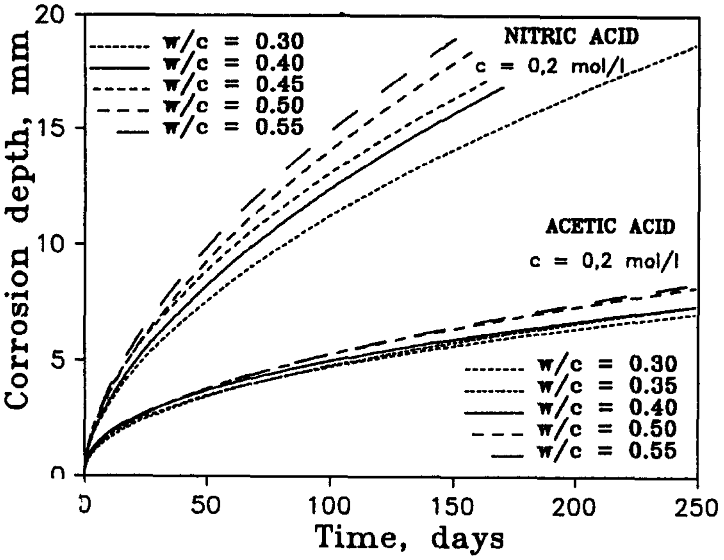

FIG. 4.
Comparison of the aggressive effects of solutions of nitric and acetic acids (Figs. 2 and 3). The curves represent graphs of equations found by regression analysis (Table 1).

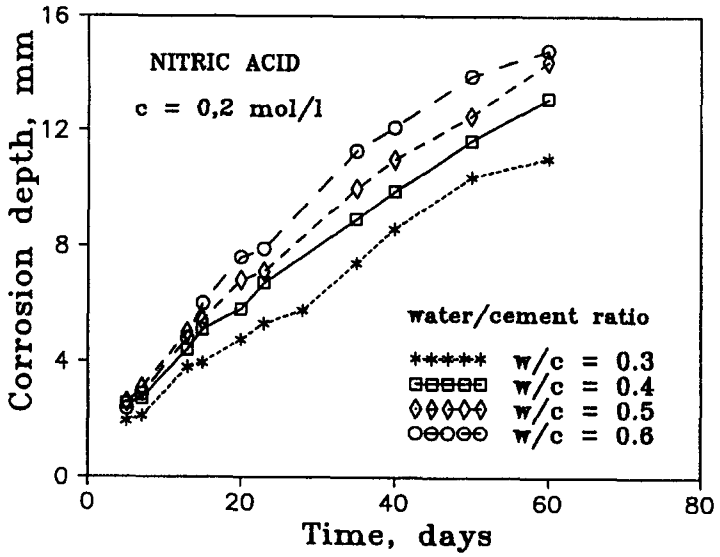

FIG. 5.
Depth of corrosion of HCP's with different w/c's related to the duration of the nitric acid solution attack (experiment III).

TABLE 1

The Equations Found by the Regression Analysis of Experimental Results Presented in Figs. 2, 3 and 5, Expressing the Corrosion Depth of HCP's with Different W/C's in Solutions of Acetic Acid and of Nitric Acid (c = 0.2 mol/l) Related to the Duration of the Attack

	Depth of corrosion, mm		
W/C	Nitric acid Experiment I	Acetic acid	Nitric acid Experiment III
0.30	$d = 0.847 \,.\, t^{0.562}$	$d = 0.626 \,.\, t^{0.440}$	$d = 0.560 \,.\, t^{0.728}$
0.35	$d = 1.040 \,.\, t^{0.540}$	$d = 0.537 \,.\, t^{0.476}$	—
0.40	$d = 0.842 \,.\, t^{0.584}$	$d = 0.691 \,.\, t^{0.430}$	$d = 0.780 \,.\, t^{0.686}$
0.45	$d = 1.015 \,.\, t^{0.555}$	$d = 0.391 \,.\, t^{0.555}$	—
0.50	$d = 0.895 \,.\, t^{0.599}$	$d = 0.586 \,.\, t^{0.478}$	$d = 0.822 \,.t^{0.699}$
0.55	$d = 0.970 \,.\, t^{0.594}$	$d = 0.550 \,.\, t^{0.493}$	
0.60	—	—	$d = 0.698 \,.\, t^{0.769}$
average value of exponent	0.572	0.478	0.720

Calculation of Coefficients A and B of Equation (18) from Experimental Results. Empirical equations expressing corrosion of an HCP with w/c = 0.4 in solutions of acetic acid and of nitric acid, have been published in part I of this paper [1]. They have the following form:

$$d = 4.11 \,.\, c^{0.7} . t^{0.56} \quad \text{- describes attack of nitric acid.} \qquad (19)$$

$$d = 1.232 \,.\, c^{0.525} . t^{0.52} \quad \text{- describes attack of acetic acid.} \qquad (20)$$

where: d - is depth of corrosion in mm,
c - is concentration of the acid solution in mol/l, and
t - is the duration of acids' action in days.

A further step in this paragraph is to extend the validity of these basic empirical equations (19) and (20), by incorporating the w/c as an additional factor affecting the rate of the corrosion process.

The generalized equation (18) can be also written in the form given by eq. (21):

$$d^{1/n} = (K_{0.4} . c^{m} . t^{n})^{1/5} . (A + B \,.\, w/c) \qquad (21)$$

and, at constant values of concentration (c) and time (t), in the form:

$$(d)_{t,c}^{1/n} = k \,.\, (A + B \,.\, w/c) = k \,.\, A + k \,.\, B \,.\, w/c = A' + B' . w/c \qquad (22)$$

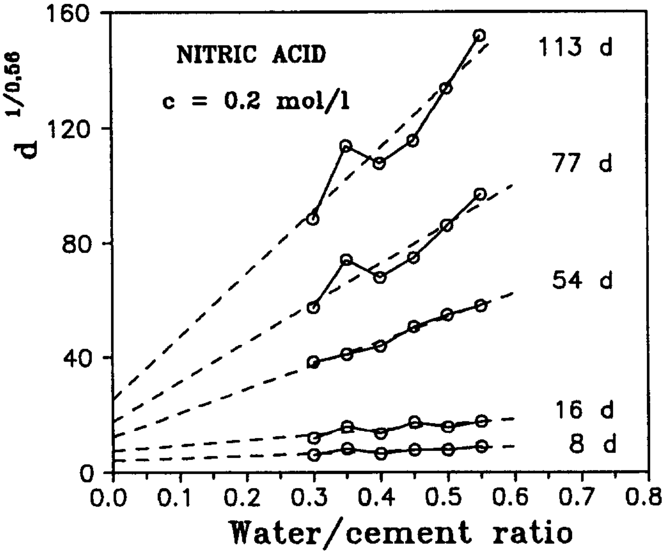

FIG. 6.
Influence of w/c on depth of HCP corrosion in a solution of nitric acid (Experiment I).

Equation (22) represents a linear function of one variable, (w/c).

Figs. 6, 7 and 8 show the experimentally based dependence of d as a function of w/c. To calculate the values of $d^{1/n}$, we used the numerical values of the exponents (n) from the empirical eqs. (19) and (20); although they differed slightly from the average values of (n) from the regression equations presented in Table 1. The lines of regression in Figs. 6, 7 and 8, expressing dependence d = f (w/c), are defined by equations in Table 2. Coefficients A' and B' in these equations increase in time. According to eqs. (21) and (22), the quotient of A' and B' equals that of A and B because:

$$\frac{B'}{A'} = \frac{k.B}{k.A} = \frac{B}{A} \tag{23}$$

Coefficients A and B, therefore, represent the constants, that are independent of time.

A. Attack of the nitric acid solution (experiment I.). Applying the same method used to get the generalized equation (18), to equation (19), leads to the extended equation (24):

$$d = 4.11 . (A + B . w/c)^{0.56} . c^{0.7} . t^{0.56} \tag{24}$$

Similarly, applying the same method to the empirical equation expressing depth of corrosion of the reference specimen with w/c = 0.4 (in Table 1), results in obtaining eq. (24.1):

$$d = 0.842 . (A + B . w/c)^{0.56} . t^{0.584} \tag{24.1}$$

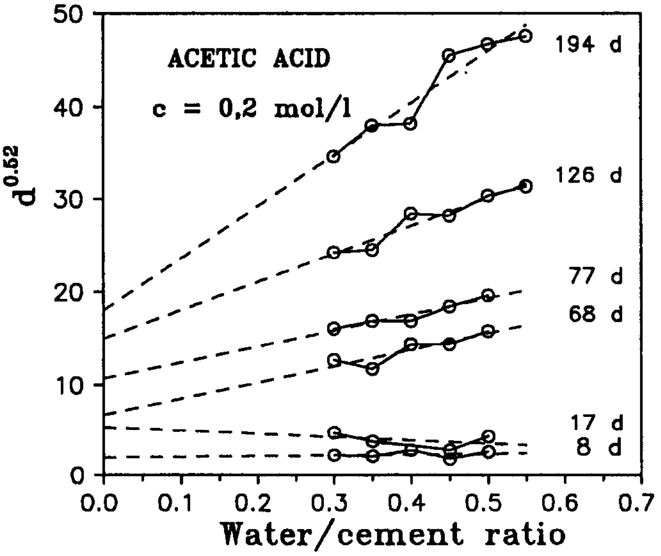

FIG. 7.
Influence of w/c on depth of HCP corrosion in a solution of nitric acid (Experiment III).

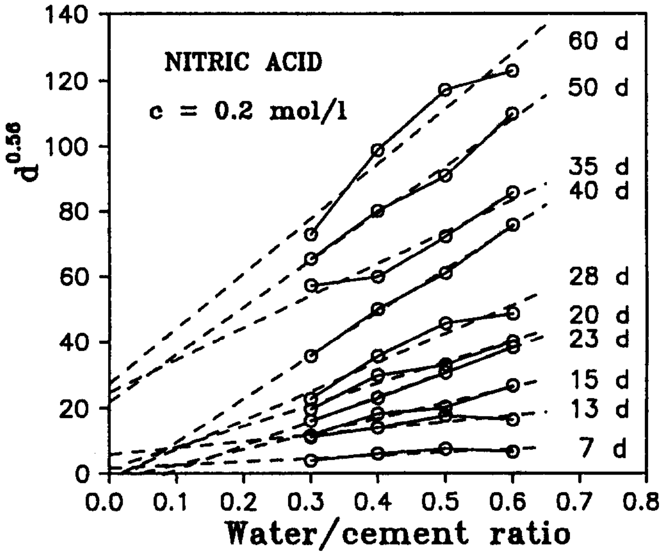

FIG. 8.
Influence of w/c on depth of corrosion of HCP's in a solution of acetic acid.

In the case where the HCP has w/c = 0.4, equations (19) and (24) should be identical. From that it follows that:

$$(A + B\,.\,0.4)^{0.56} = 1 \qquad (25)$$

Coefficients A and B can than be calculated by solving a set of two equations in two unknowns. For example, from the value of B'/A' at 8 days of corrosion of HCP's in nitric acid solution - experiment I, (the first line in Table 2), and with use of equation (25), also taking into account eq. (23), we get two equations in two unknowns (26):

TABLE 2

Regression Equations from Figs. 6, 7 and 8,
Proportion of Regression Coefficients B'/A', and Values of Coefficients A and B
Found by Solving Two Equations in Two Unknowns Using Eq. (26)

Nitric acid (c = 0.2 mol/l) Experiment I (Fig. 6)

Time (days)	Line of regression (A + B.w/c)	B/A	A	B
8	4.143 + 7.976.w/c	1.925	0.565	1.088
16	7.531 + 18.424.w/c	2.446	0.505	1.236
54	12.342 + 83.163.w/c	6.738	0.271	1.823
77	17.670 + 137.615.w/c	7.788	0.243	1.892
113	25.280 + 219.313.w/c	8.676	0.224	1.941

Nitric acid (c = 0.2 mol/l) Experiment III (Fig. 7)

7	1.667 + 9.766.w/c	5.858	0.299	1.752
13	5.882 + 19.876.w/c	3.379	0.425	1.437
15	-2.053 + 47.363.w/c	-23.067	-0.122	2.804
20	-6.236 +73.961.w/c	-11.861	-0.267	3.168
23	1.633+ 64.544.w/c	39.522	0.060	2.351
28	-1.261 + 87.611.w/c	-69.477	-0.037	2.593
35	-3.634 + 131.821.w/c	-36.275	-0.074	2.685
40	-24.774 + 97.976.w/c	3.955	0.387	1.532
50	21.805 + 144.071.w/c	6.607	0.275	1.814
60	27.302 + 168.161.w/c	6.159	0.289	1.778

Acetic acid (c = 0.2 mol/l) (Fig. 8)

8	1.971 + 0.841.w/c	0.427	0.854	0.364
17	5.372 - 3.629.w/c	-0.676	1.370	-0.926
68	6.742 + 17.649.w/c	2.618	0.489	1.279
77	15.029 + 30.194.w/c	2.009	0.554	1.114
126	10.725 + 17.147.w/c	1.599	0.610	0.975
194	18.011 + 55.913.w/c	3.104	0.446	1.385

TABLE 3

Values of Coefficients A and B.
The "Theoretical" Ones Were Calculated Using Eqs. (11) and (12);
The "Empirical" Ones Represent the Average Experimental Values from Table 2

	Values of coefficients A, B			
	Theoret., calculated by eqs. (11) and (12) (ρ_c = 3100 kg/m3)	Nitric acid Experiment I	Nitric acid Experiment II	Acetic acid
A	0.446	0.224	0.124	0.720
B	1.384	1.941	2.191	0.699

$$\left.\begin{array}{l} \left(\frac{B}{A}\right)_{8\,\mathrm{days}} = 1.925 \\ \underline{A + B.0.4 = 1} \end{array}\right\} \qquad (26)$$

Values of A and B, found by solving the complete set of two equations in two unknowns, are given in Table 2. Because values of A decrease and those of B increase with time, the average values of A and B can hardly be taken as representative ones. Therefore the values of A and B of the last test were taken as the most representative ones (Table 3).

B. Attack of the acetic acid solutions. Applying the same method as mentioned above to eq. (20), results in obtaining the extended equation (27):

$$d = 1.232\,.\,(A + B\,.\,w/c)^{0.52}.c^{0.525}.t^{0.52} \qquad (27)$$

Coefficients A and B can be then calculated with the use of values of the quotients B'/A' in Table 2 and with use of eq. (25), by solving the set of two equations in two unknowns. The results are presented in the Table 2; the average values are presented in Table 3.

C. Comparison of obtained values of coefficients A and B. In Table 3 the average values of the empirically obtained coefficients A and B from Table 2 are presented together with the "theoretical" values of A and B, calculated by eqs. (11) and (12). Taking different pairs of coefficients A and B from Table 3, we calculated values of the factor W = (A + B.w/c) of eq. (18). Graphs of W versus w/c of HCP's are shown in Fig. 9. Figure 9 shows, that the influence of w/c depends on type of attacking acid. In nitric acid solution the influence of w/c appears to be greater, than in solution of acetic acid. The "theoretical" influence of w/c is represented by lines, which are located between the "empirical lines" of nitric acid and acetic acid. Fig. 9 also shows values of $d_{w/c}/d_{0.4}$, representing quotients of the corrosion depth of HCP's with varying values of w/c, and the corrosion depth of the HCP w/c = 0.4. Taking eq. (24) and eqs. (19) or (25), as well as eqs. (27) and (20), we may write the quotient $d_{w/c}/d_{0.4}$ in the following general form:

$$\frac{d_{w/c}}{d_{0.4}} . 100 = (A + B . w/c)^n . 100 \qquad (28)$$

Figure 9 further shows that in nitric acid solutions the difference in corrosion depths between an HCP with w/c ratio of 0.6 and that of 0.4 is about 20–22%. In solution of acetic acid the difference represents about 7%. The theoretical "prediction" is about 14%, which represents approximately the average value of the above mentioned experimental data.

We made the final evaluation of the results by calculating the corrosion depth of HCP's with different w/c by using coefficients A and B from Table 3 (attack of nitric acid, exp. I) and equation (24.1). Comparison of the calculated values, presented in Fig. 10, with the experimental ones, in Fig. 4, shows no relevant differences.

5. Conclusion

1. The rate of corrosion decreases with an increase in cement content per unit volume of HCP (increases with w/c).

2. The w/c was found to have only a limited influence on the corrosion rate of HCP's. This limitation is given by the range, in which the values of w/c of HCP's usually vary. For example, an HCP with w/c = 0.7, exposed to an attack of the nitric acid solution, is expected to corrode to the depth about 50% bigger, than an HCP with w/c = 0.3 in the same period of time. In the acetic acid solution the expected difference is about 15%.

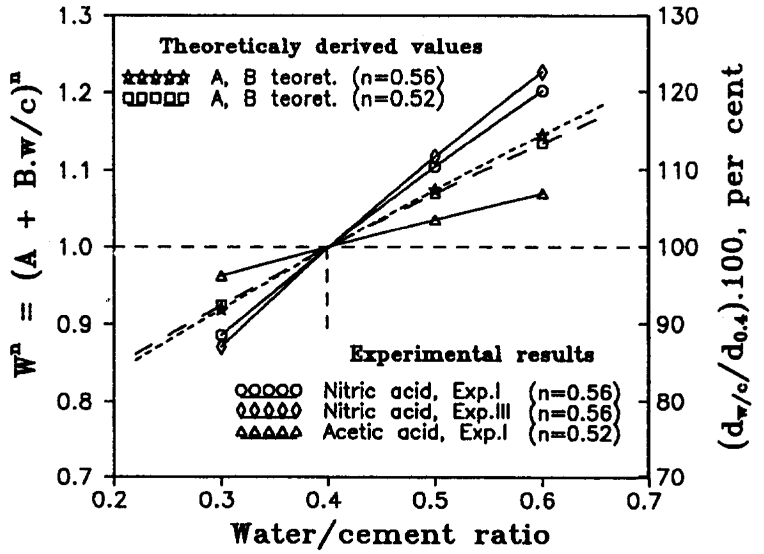

FIG. 9.

Factors W^n calculated from different pairs of coefficients A and B (Table 3) and their dependence on the w/c of HCP's. The lines also represent quotients $d_{w/c}/d0.4$ where $d_{w/c}$ is corrosion depth of an HCP with water/cement ratio w/c, and $d_{0.4}$ is corrosion depth of HCP with w/c = 0.4.

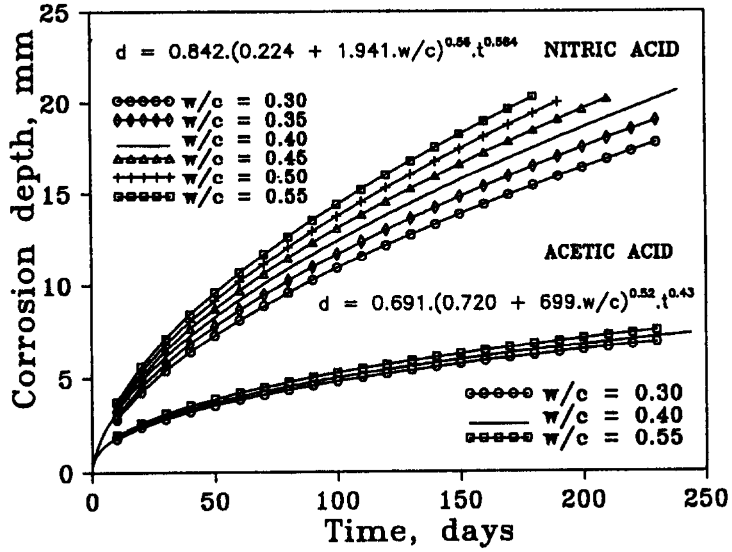

FIG. 10.

Influence of w/c on the corrosion depth of HCP's. The points represent calculated values using a factor W. (Compare with Fig. 4)

References

1. V. Pavlík, Cem. Concr. Res. 28, 1495 (1994).
2. A. Bajza, Symposium Proc., Pore Structure and Permeability of Cementitious Materials. Pittsburgh, MRS 1989, Vol. 137, pp. 325–334 (1989).
3. A. Bajza, Proc. 9th Intl. Cong. Chem. Cement. New Delhi, National Council for Cement and Building Materials 1992, Vol. V, pp. 402–408 (1992).
4. A. Bajza and I. Rouseková. FIP Symposium '92, Budapest, Complementary Vol., Hungarian Scient. Soc. for Building. pp. 275–280 (1992).
5. L. Q. Hung, Dissertation thesis. Faculty of Civil Engineering, Slovak Technical University, Bratislava (1988).
6. S. Unčík, Dissertation thesis. Faculty of Civil Engineering, Slovak Technical University, Bratislava (1989).
7. L. Romben, CBI forskning research 1:78 und 9:79, Cement- och betong instituted, Stockholm.
8. V.M. Moskvin, F.M. Ivanov, S.N. Alexejev and E.A. Gusejev. Corrosion of concrete and reinforced concrete, methods of their protection (in Russian), p. 536. Strojizdat, Moscow (1980). (cit. in [3]).
9. H. Grube und W. Rechenberg, Beton 37, 446 (1987).
10. H. Grube and W. Rechenberg, Cem. Concr. Res. 19, 783 (1989).
11. N.I. Fattuhi and B.P. Hughes, Cem. Concr. Res. 18, 545 (1988).
12. V. Pavlík, Cem. Concr. Res. 24, 551 (1994).