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Porous structure of the ITZ around galvanized and ordinary steel reinforcements

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Abstract

The use of galvanized bars is one of the solutions recommended to avoid corrosion of reinforced concrete structures. The reaction between the galvanized coating and the wet concrete produces zinc hydroxide, and subsequently calcium hydroxyzincate, accompanied often by the evolution of hydrogen. The tests carried in this study show, 19 h after casting, a modification of the pore size distribution and an increase in porosity of the interfacial transition zone (ITZ) between the cement paste and the galvanized steel, in comparison with the ITZ of cement paste–steel contact surface. However, the characteristics of the ITZ change over time: at the test period of 28 days, the porous structure of the ITZ around galvanized and ordinary steel is not significantly different. This difference decrease is due to the formation of calcium hydroxyzincate. Calcium hydroxyzincate favors the hydration at the ITZ. This compound, as well as cement hydration products can fill the porous structure in this zone. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Interfacial transition zone; Mercury porosimetry; Pore size distribution; X-ray diffraction; Microstructure; Cement paste; Zinc

1. Introduction

Steel in concrete is passivated in the pore solution concrete (pH ~ 12–13) by iron oxide film. Due to carbonation or by action of chloride ions, this passive film may be destroyed. As the iron corrosion products occupy more space than steel, the cracking and the spalling of the cover concrete are induced. As a result, the service life of the concrete structure is reduced.

To avoid corrosion of the reinforcements, a protective coating of the rebars by galvanizing is suggested. Galvanized coating acts as a barrier to chloride attack. Additionally, the sacrificial action of the zinc protects the steel.

In reinforced concrete structure a water/cement ratio gradient develops around the aggregates and the reinforcements, resulting in the modification of the microstructure of the surrounding hydrated cement paste. This modified zone is called "interfacial transition zone" or ITZ [1]. When galvanized reinforcements are used, a chemical reaction occurs between the superficial layer of the coating and the ions of the pore solution concrete. This interaction results in the delay of the interfacial concrete hydration and is often accompanied by the formation of hydrogen at the interface [2,3]. This can produce local porosity in the interfacial concrete and change the microstructure of the ITZ.

The object of this work is to study the incidence of the interaction between galvanized steel and pore solution concrete on the porous structure of the interfacial concrete. That for the pore size distribution and the water absorption of cement pastes cast on galvanized steel or naked steel plates are compared. Analyses by X-ray diffraction (XRD) are also performed on steel–cement paste and galvanized steel–cement paste contact surfaces.

2. Type of test specimens

Specimens of 40 × 80 × 40 mm are made by casting a cement paste on naked steel or galvanized steel plate. The hot-dip galvanized steel plates have a coating thickness of 80 μm (Fig. 1).

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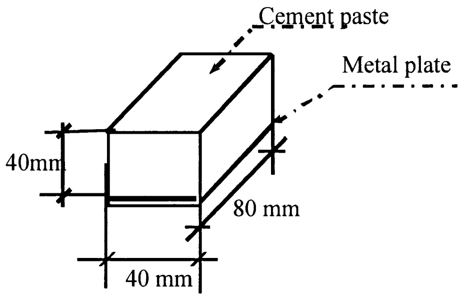

Fig. 1. Test specimen.

The cement paste is made from rapid-hardening Portland cement CPA CEMI 52.5 R with water/cement ratio of 0.5. The chemical composition of the cement used is given in Table 1.

After 19 h (or 28 days) of cure in fog room, these specimens are broken mechanically at the metal plate–cement paste interface. Each cement paste sample is then stoved until it reaches constant mass.

For every test period (19 h or 28 days), the pore size distribution and the water absorption are determined on two identical specimens cast on each metal support (naked steel or galvanized steel).

3. Pore size distribution

3.1. Experimental method

To determine the pore size distribution of the ITZ, a mercury intrusion porosimeter is used. The principle is based on the intrusion of a nonwetting liquid (mercury) in a porous network, by applying pressures from 0.1 to 60,000 psi. The average radius r of the pore, considered cylindrical, reached by pressure P_c is determined by the Washburn equation:

$$r = \frac{-2\sigma\cos\theta}{P_c}$$

where r is the average radius of the pore, σ is the surface tension of mercury ($\sigma = 0.474$ N/m), θ is the contact angle ($\theta = 130°$), and P_c is the operating pressure.

The results are presented in porosimetric curves deferring, for a given porous space, the variation of mercury intrusion volume reported to the total volume of mercury injected in the network with the average diameter determined from the Washburn equation.

Table 1
Chemical composition of the cement used

SiO_2	Al_2O_3	Fe_2O_3	CaO (free)	MgO	SO_3	Na_2O	K_2O	PF
20.25	5.04	2.40	64.80 (0.30)	1.83	3.1	0.06	0.50	2.00

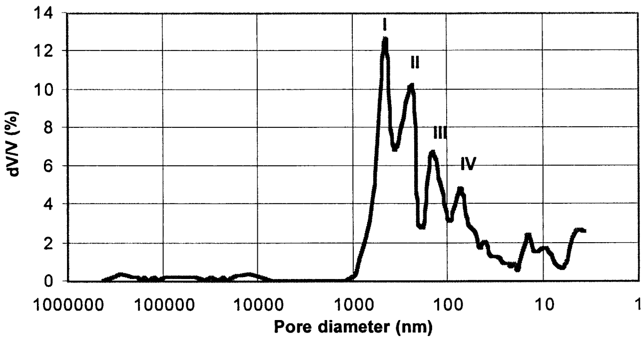

Fig. 2. Pore size distribution of the bulk cement paste at 19 h after casting.

3.2. Preliminary study

The objective of the study is to compare the porous structure of the cement paste–steel and the cement paste–galvanized steel contact surfaces. We must first determine the thickness of the zone affected by the chemical reaction between the zinc and the pore concrete solution.

At 19 h after casting, the test specimens made with steel or galvanized steel plates are broken. Once the cement pastes are stoved, three different thicknesses (1.4, 0.8 and 0.5 mm), and therefore masses (respectively 1.25, 0.76 and 0.45 g) of samples are collected at the interface.

The pore size distributions of three samples from the same base plate with the same basic surface but with different thickness are thus compared. The pore size distribution measured on a core of bulk cement paste is taken as reference. The reference curve (pore size distribution of the bulk cement paste) is given in Fig. 2. It indicates the presence of four groups of capillary pores, corresponding to average diameters of 450, 230, 140 and 70 nm; the gel pores are not accessible to mercury intrusion porosimetry. These groups of capillary pores are designed, respectively, by I, II, III and IV on Fig. 2.

Fig. 3 shows the pore size distribution of the samples collected at the steel plate–cement paste contact surface. Samples 1, 2 and 3 have also different thicknesses but identical basic surfaces. Their mass is, respectively, 1.25, 0.76 and 0.47 g.

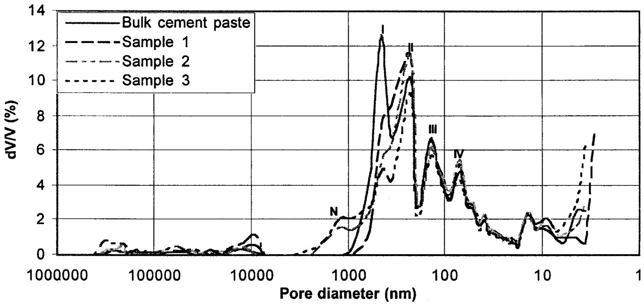

Fig. 3. Pore size distribution of samples collected at the cement paste–steel contact surfaces at 19 h after casting.

This figure indicates a change in the average pore diameter of capillary pores of the Groups I and II. A new group with average diameter of 1000 nm is also observed (Group N on Fig. 3). The Groups III and IV remain unchanged.

Fig. 4 shows the pore size distribution of three samples collected at the galvanized plate–cement paste surface. The average diameter of the first group became larger (600 nm, Group A on Fig. 4) and no change is observed for the finer capillaries (Groups II, III and IV on Fig. 4).

At last, this preliminary study indicates that the pore size distribution of the interfacial zone formed on the studied metal plates (steel and galvanized steel) is different when the average pore diameter is greater than 230 nm (pores larger than the capillaries of Group II). Moreover, it shows that the sample thickness affects the measured pore size distribution: the porosimetric curve of a too-thick sample collected at the interfacial zone is not very different from that of the bulk cement paste. We can conclude therefore that, in our conditions, a sample thickness lower than 1 mm is necessary to study the porous structure of the ITZ.

3.3. Comparative study

To study the incidence of the galvanized coating, the pore size distribution of the samples collected in the vicinity of galvanized steel or steel plate (samples no. 3) are compared (Fig. 5).

In the case of steel–cement paste contact, for the test period of 19 h, and when the samples are collected in the ITZ, a new group of capillaries, with an average pore diameter of 1000 nm, is noticed (Group N on Fig. 5). Buil and Ollivier [4] observed the same range of pore size (between 50 and 1000 nm) in mortars. The authors explain these particular pores by the presence of aggregates. The cement paste surrounding the aggregate is more porous than the bulk cement paste [4,5]. In the case of our study, the pore diameter of 1000 nm is attributed to the spaces formed in the interfacial zone in contact with the steel plate, due to the wall effect. This effect induces also the removal of the pore population of Group I.

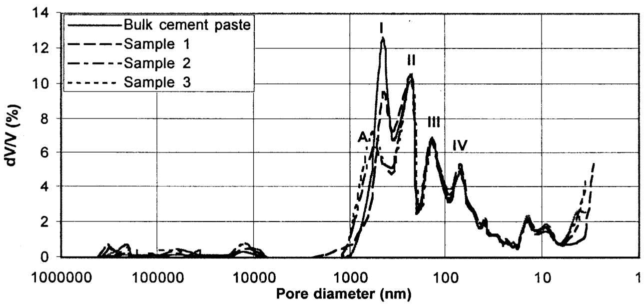

Fig. 4. Pore size distribution of the samples collected at the cement paste–galvanized steel contact surface at 19 h after casting.

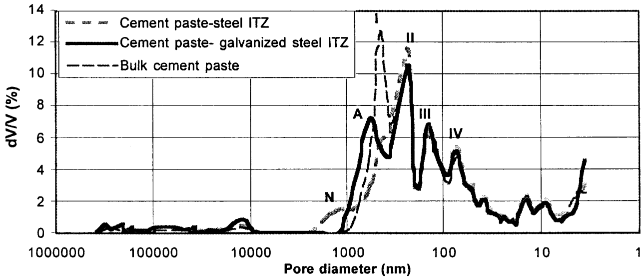

Fig. 5. Pore size distribution of the ITZ, 19 h after casting.

When galvanized plate is used, the superficial coating reacts with the aqueous phase of the cement paste and we can notice the presence of an adherent film of paste on the plate surface. The effect of water/cement gradient increase is not as important as in the case of the cement paste–steel interface. Moreover, Fig. 5 shows that a part of pores of Group I move to larger diameters (Group A on Fig. 5) when the ITZ is in contact with the galvanized plate. The average pore diameter of the population of Group A is thinner than that of Group N, but the population of Group A is greater.

The difference between the network of the ITZ in contact with galvanized steel and steel is due either to the presence of a network of hydrogen bubbles interconnected with the capillary pores of the paste, or to the delay of the hydration (filling of the spaces between cement grains). However, no significant difference is noted in the pore size distribution of the thinner capillaries (pore diameter smaller than 230 nm).

When hydration proceeds in cement paste, the hydration products fill the spaces and reduce the capillary size [4,6]. So, we studied the pore size distribution of steel–cement paste and galvanized steel–cement paste ITZ 28 days after casting (Fig. 6).

This figure shows that the capillary size decreases, whatever the nature of the metal plate used (galvanized steel or steel). Moreover, the pore size distribution of the studied interfaces does not show any significant difference on the contrary at 19 h of age (Fig. 5). Cement hydration products have probably filled the pores affected by the

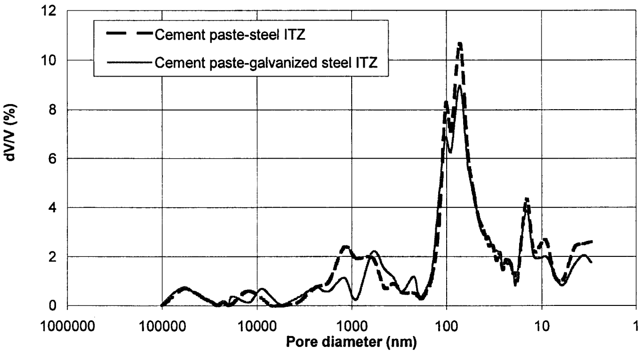

Fig. 6. Pore size distribution of the ITZ, 28 days after casting.

interaction between cement and galvanized steel. However, the pores due to the wall effect (spaces formed in contact with the steel plate) remain present even at 28 days. This corresponds to the previous results [4,5], indicating the presence of these specific pores of the ITZ in the mortars with water/cement ratio of 0.4 at 3 months.

The results indicate that the pore size distribution of the studied ITZ depends on the metal plate used (steel or galvanized steel), specially 19 h after casting.

To confirm the results of mercury porosimetry, water absorption tests are performed.

4. Water absorption

4.1. Experimental method

Water absorption test characterizes the ability of a porous material to absorb and transmit wetting liquid (water) by capillarity. The theoretical bases are established from the theory of permanent rate of flow in unsaturated and unidirectional porous materials [7,8].

In this work, cement paste specimen of 40 × 80 × 40 mm casted on naked steel or galvanized plate are tested. To determine the ability of the ITZ to absorb water, side faces of dry cement paste which were in contact with plates (galvanized steel or steel) are coated with resin. The face in contact with the metal plate is placed in contact with free water of 1 cm height; the water surface is kept at a constant level by an overflow. The water mass absorbed by the sample is measured at successive determined times. The total duration of the test is 24 h.

The coefficient representing the water quantity absorbed per porous material surface unit and per time unit is defined as follows [7,8]:

$$a = \frac{\Delta m}{A\sqrt{t}}\rho_{\mathrm{water}}$$

(a is expressed in kg m^{-2} $\mathrm{s}^{0.5}$ or in kg m^{-2} $\mathrm{h}^{0.5}$)

where Δm: water quantity absorbed by the porous material, ρ_{water}: water density, A: contact surface with water (m^2), and t: suction time (s or h).

The capillary suction follows Laplace's law. In a capillary the pressure difference across the air/water interface is given by the relation:

$$P = P_{\mathrm{air}} - P_{\mathrm{water}} = \frac{2\sigma\cos\theta}{r}$$

where r is the average radius of the capillary, σ is the surface tension, and θ is the angle of contact of air/water.

When this pressure, due to the capillary forces, is balanced by the weight of column of the absorbed water in the capillary, the water reaches the maximum height in the capillary and the water absorption phenomenon stops. Jurin's law gives the maximum height $H_{\max}$ of the absorbed water in the capillary:

$$H_{\max} = \frac{2\sigma\cos\theta}{\varpi_{\mathrm{e}} r}$$

where ϖ_{e} is the voluminal weight of water.

The water absorption phenomenon in porous building materials (mortar or concrete) is generally modeled by a linear relationship between the cumulative absorbed water (per unit area of the inflow surface) i and the square root of the elapsed time t [7,8]:

$$i = St^{1/2},$$

where S is the sorptivity of the material.

The volume of the absorbed water in a porous material is given by $V = k_1\, r^{5/2} t^{1/2}$ [9]. As the capillaries are considered as cylindrical pores, the height of absorbed water is given by:

$$h = (k_1/\pi) r^{1/2} t^{1/2}$$

where k_1 characterizes the interstitial liquid (water) by it dynamic viscosity, surface tension and the angle of contact of air/liquid.

The sorptivity of a porous material is as great as the average radius of the capillary is largest, although the capillary forces are inversely proportional to the capillary radius.

From these formulas, a calculus shows that after 1 h, capillaries coarser than 12 μm are not concerned by water absorption.

The results of the water absorption test are presented in absorptivity curve, deferring the water quantity absorbed per porous material surface with the square root of elapsed time.

4.2. Results of water absorption test

At the period test of 19 h, the curves obtained for the cement pastes that were in contact with galvanized steel or steel are similar until a quarter of an hour and then deviate progressively (Fig. 7). After 30 min, this difference became more significant.

Two slopes characterize the curve representing the water quantity absorbed by unit area versus $\sqrt{t}$. The first one is due to the important quantity of water absorbed by both coarser

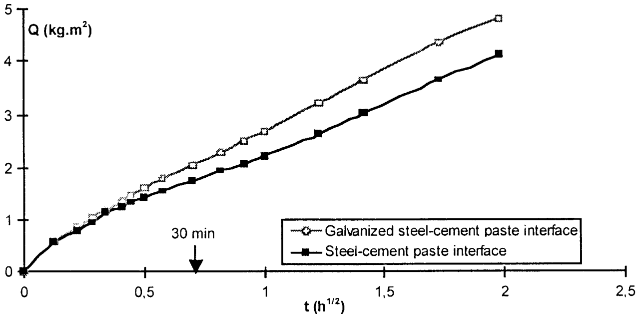

Fig. 7. Absorptivity curve at 19 h.

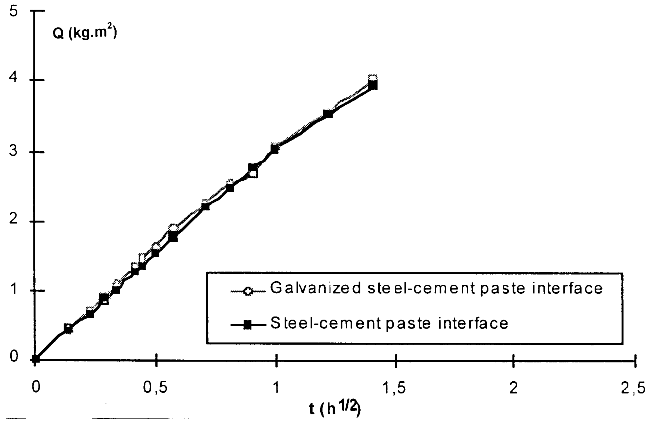

Fig. 8. Absorptivity curve at 28 days.

and thinner pores of the test specimen. After a test period of 30 min, the radius of the coarser capillary concerned by the water absorption is equal to 15 μm, pores coarser than this value are saturated. The second slope characterizes the water penetration in thinner capillaries which remain concerned by the water absorption. Fig. 7 shows that in this last case, the sorptivity of the paste in contact with galvanized plate is greater than that of the paste in contact with steel.

This difference is attributed to the pore size distribution of the ITZ: the population of Group A (ITZ in contact with galvanized steel) is larger than that of Group N (ITZ in contact with steel).

For the 28-day-old specimens, the absorptivity curves of steel–cement paste and galvanized steel–cement paste are similar (Fig. 8). This result indicates a modification of the pores network, and so of the microstructure of the interface. To complete this study, analyses by XRD of the interfacial zone studied are performed.

5. XRD analysis

5.1. Experimental method

XRD technique is used in order to identify the compounds formed at the interface between galvanized steel (or steel) plate and the cement paste.

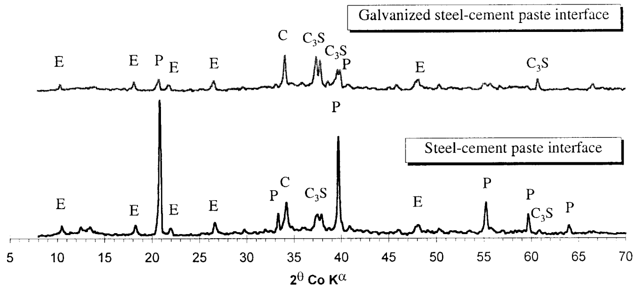

Fig. 9. X-ray diffractograms of the ITZ at 19 h. P: portlandite; E: ettringite; C: calcite.

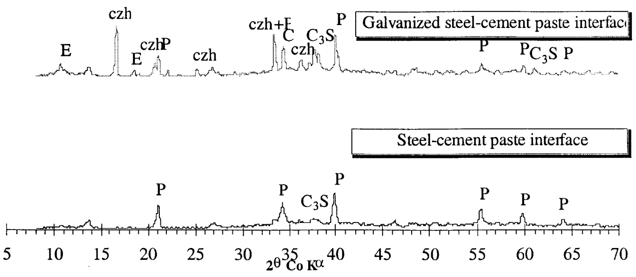

Fig. 10. X-ray diffractograms of the ITZ at 28 days. czh: calcium hydroxyzincate; P: portlandite; E: ettringite; C: calcite.

Specimens cast as presented in Section 2 are used. After a curing period of 19 h (or 28 days), they are broken at the interface. Test specimens of 20 × 20 mm are then cut from the cement paste of the specimens and X-ray analyses are performed on the cement paste face that was in contact with the metal.

5.2. Results of X-ray analysis

At 19 h, XRD analysis of ITZ in contact with galvanized steel shows the presence of anhydrous compounds (silicate tricalcique C_3S) and hydrated products: portlandite $Ca(OH)_2$ and ettringite $3CaO$, Al_2O_3, $3\ CaSO_4$, $32\ H_2O$. These compounds are also identified at the ITZ in contact with steel (Fig. 9). The intensity of the principals rays of the above compounds seems to depend on the nature of the metallic plate (galvanized steel or steel). However, the intensity of rays must not be compared directly, a little difference in preparation or/and installation of test specimens can induce a significant variation of the intensity. Moreover, crystals of portlandite formed at the interface can be oriented when the test samples are prepared for X-ray analyses. However, precedent results indicate a delay of hydration of the cement paste in contact with zinc in comparison with the paste in contact with steel [2].

At 28 days, the most interesting fact is the appearance of a new compound: calcium hydroxyzincate $Ca(Zn)_2(OH)_6$, $2H_2O$ at the interface in contact with galvanized steel (Fig. 10). This result agrees with precedent studies [2], where the authors show the retarding effect of zinc on the hydration of C_3S. The delay is explained by the precipitation of an amorphous layer of zinc hydroxide around the anhydrous grains and it is shown that the hydration reaction starts again when the transformation of the zinc hydroxide into the crystalline calcium hydroxyzincate occurs [2,3].

6. Discussion

At 19 h after casting, the results of mercury porosimetric tests indicate that the porous structure of the ITZ depends on the nature of the plate used (galvanized steel or steel). However, the test specimen may be correctly collected. If a thickness of the sample is too important the size distribution of the bulk cement paste will be analyzed instead of the interfacial zone. In our experimental conditions (water/cement ratio, composition of the cement used, exposition conditions...) the critical thickness is approximately 1 mm. This critical value is the thickness of the interfacial zone concerned by variation, due to the chemical interaction between cement paste and zinc, of the network of capillaries with a pore radius between 500 and 50 nm.

It is important to specify that this value is different than the thickness of the zone affected by the chemical reaction, the pores formed in this last zone can be interconnected to the bulk paste and increase the total zone concerned by the variation of the network structure.

The water absorption tests confirm the influence of the metal nature on the porous structure of the ITZ. For capillaries less than 15 μm, the sorptivity of the paste in contact with galvanized steel is more important than that with the paste in contact with steel.

At 28 days, the absorptivity curves of galvanized steel–cement paste and steel–cement paste ITZ are similar. Moreover, no significant difference in the pore size distribution of these contact surfaces is observed with the porosimetric analyses.

The analyses by XRD of the ITZ studied indicate crystallization of calcium hydroxyzincate at the interface between galvanized steel and cement paste at 28 days. The crystallization of this compound breaks down the amorphous layer around the anhydrous grains and allows the hydration of cement paste to start again [2,3].

The progression over time of the porous structure of the ITZ between galvanized steel and cement paste is conditioned by crystallization of calcium hydroxyzincate, which depends strongly on the chemical reaction that is liable to occur [10,11]. When it is possible, like in the case studied, the renewal of the cement hydration reduces the pore size by filling it with hydration products.

However, it is difficult to conclude on the cause of modification of the porous structure. We can explain this either by the capillary pores formed in the zone delayed by the chemical reaction, or by the bubbles formed during the hydrogen release (if those are interconnected with the porous network). Moreover, if hydrogen is trapped in isolated bubbles, the whole associated porosity cannot be accessed by water or by mercury.

7. Conclusions

The results obtained reveal that the galvanized coating affects the porous structure of the ITZ with the surrounding cement paste.

However, the crystallization of calcium hydroxyzincate favors the filling over time of interfacial zone hydration and this difference with the ITZ at the cement contact with steel is vanished at 28 days of age.

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