Corrosion Mechanism and Bond-Strength Study on Galvanized Steel in Concrete Environment

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Zinc coating on carbon steels give the higher corrosion resistance in chloride containing environments and in carbonated concrete. However, hydrogen evolution accompanies the corrosion of zinc in the initial activity in fresh concrete, which can lead to the formation of a porous structure at the reinforcement -concrete interface, which can potentially reduce the bond-strength of the reinforcement with concrete. The present study examines the mechanism of the corrosion of hot-dip galvanized steel in detail, as in the model pore solutions and real concrete. Calcium ion plays an important role in the corrosion mechanism, as it prevents the formation of passive layers on zinc at an elevated alkalinity. The corrosion rate of galvanized steel decreases in accordance with the exposure time; however, the reason for this is not the zinc transition into passivity, but the consumption of the less corrosion-resistant phases of hot-dip galvanizing in the concrete environment. The results on the electrochemical tests have been confirmed by the bond-strength test for the reinforcement of concrete and by evaluating the porosity of the cement adjacent to the reinforcement.

Keywords: concrete reinforcement, galvanized steel, bond strength, porosity

1. Introduction

Hot-dip galvanized steel is one of the low-cost concrete reinforcing materials when increased durability of a re-inforced concrete structure is required while avoiding any costly repairs. Like the various types of stainless steels, galvanized steel is also expected to have higher corrosion resistance towards chlorides compared to ordinary carbon steel and maintaining the passive state after carbonation of concrete cover. Published data on the appropriateness of using galvanized steel, however, are contradictory. The main disadvantage of galvanized steel is hydrogen evolution accompanying the corrosion of zinc in the activity in fresh concrete. Due to hydrogen, the cement paste has porous structure, which can result in a reduction in bond-strength with concrete reinforcement. Later, when porous concrete solidified, galvanized steel goes into passivity. The high corrosion rate at the beginning is also seen as positive as insoluble zinc salts being formed in the pores of the concrete reportedly reduce the perme-ability of concrete for corrosion stimulators and the bond-strength with reinforcement over time compared to the bond-strength with carbon steel even increases [1].

1.1 Zinc corrosion as a function of pH

The dependence of the corrosion behaviour of zinc on pH without the presence of calcium ions appears to be clear from the published data. Up to pH 12.7 (0,05 mol·l⁻¹ KOH or NaOH), the galvanized steel is passive from the beginning of exposure [1], which refers to free corrosion potential (E_{corr}) more positive than −800 mV(SCE), and free corrosion current densities derived from polarization resistance are of the order of tens of mA·m⁻². Lower corro-sion resistance and localized corrosion were identified at pH lower than 12 [3]. At pH 12.8 (up to13.8), the galvan-ized steel is active originally (E_{corr} approximates to −1400 mV(SCE). Such active corrosion is accompanied with hy-drogen gas evolution. Passivation might be reached within 4 days if the pH is 13, at higher pH, however, the corro-sion rate reduces to the tenths of millimetres after 20 days. It is questionable of course, if the zinc coating is preserved in sufficient quality after such a long exposure time. The authors [3] accept that the zinc coating might be already dissolved and the substrate steel is the material that passivates.

1.2 Zinc corrosion at presence of calcium cathions

The corrosion behaviour of zinc and its dependence on pH change when calcium ion is present [4]. The galvan-

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ized steel effectively passivates at pH lower than 13.3. The time to passivation increases from 2 days (pH 12.6) to 10 days (pH 13.2). The probable reason for the loss of passivity at pH above 13.3 is a reduced solubility of $Ca(OH)_2$. There is not enough of calcium cathions for formation of protective $Ca(Zn(OH)_3)_2 \cdot 2H_2O$ [4]. The galvanized steel in model solutions based on $Ca(OH)_2$ up to pH 12,6 does nor passivate immediately, but after 3 days of exposure [3]. High corrosion rates were detected even at lower pH than 12 [3]. The delayed passivation cannot be explained by disclosing the Fe-Zn interlayer or substrate steel, because passivation occurs also at the specimen of pure zinc [5].

1.3 Zinc corrosion as a function of coating microstructure

At highly alkaline environment (pH > 13.4; free of Ca^{2+}), corrosion rate decreases after significant reduction of zinc coating as consequence of either complete dissolution of the coating leaving the steel substrate or leaving the bottom Fe-Zn phase layer [2,4]. At pH 13.2, just the upper most layer η is being dissolved, while at pH 13.0 is even this layer only partially dissolved [2,4]. The alloy Fe-Zn layers are probably more resistant to dissolution compared to pure zinc in the environment of pH 13.2. However, higher resistance of the alloy layers is not self-evident from the available information [5]. The alloy Fe-Zn layer that is formed at high-silicon steel exhibits lower hydrogen reduction overpotential compared to pure zinc which might increase corrosion rate of the coating [6].
Hydrogen that is formed as a consequence of active zinc corrosion increases the porosity of the cement binder. Application of galvanized steel reinforcement might affect the bond-strength with concrete, eventually. Further, quality of the zinc coating would suffer from its corrosion in active state [7,8].

1.4 Bond-strength

The bond-strength of the reinforcement is understood as a sum of all factors that limit a movement of the reinforcement when a structure is loaded (according the Czech standard CSN 73 1328 – Determination of adhesion of steel to the concrete using both the ribbed and plain

bars) [9]. The total bond-strength is given by adhesion, friction and interlacing (impact of surface geometry). If zinc corrosion affects the properties of the superficial cement binder, the adhesion factors is mostly affected as well. For objective estimation of zinc corrosion impact on the adhesion to concrete it is essential to consider and test rib-less reinforcement so that the results are not affected by the bulk mechanical properties of concrete.

The aim of this study was to identify the impact of pH and presence of calcium ion in model concrete pore solution on passivity of zinc and galvanized steel. The corrosion behaviour of the Zn-Fe intermetallic phases was also considered. Bond-strength and the porosity of the interface cement binder were evaluated for both the galvanized steel and pure zinc.

2. Experimental Procedure

Four parallel specimens were used for studying of the influence of pH and presence of calcium ions on corrosion behaviour of zinc. The specimens were exposed in KOH water solutions with pH of 12.6, 13.0 and 13.5 respectively (calcium ion free environment), and in saturated $Ca(OH)_2$ solution, the pH of which was set to 13.0 or 13.5 by addition of KOH solution. The zinc or galvanized steel flat specimen served as a bottom of a polypropylene cell with integrated graphite counter electrode and reference electrode made of activated titanium [10,11]. The exposed surface area was 255 mm^2. Zinc specimens were made of cast zinc. The chemical compositions of carbon steels for hot-dip galvanizing and the structure of the coating at the galvanized steel specimens are showed in Table 1 and Fig. 1, respectively. The chemical analysis was focused of the admixtures that affect properties of the coating, especially silicon and phosphor. The analysis was performed by means of roentgen fluorescence thus the carbon content is not involved.

Corrosion behaviour was evaluated by means of E_{corr} that was recorded during six day exposure. Polarization resistance was measured after 15 minutes and at the end of exposure by means of linear polarization in the range of ±10 mV vs. E_{corr} with scan rate of 0.1 mV·s^{-1}. All values of potential is this paper are referred to saturated calo-

Table 1   Chemical compositions of carbon steels for hot-dip galvanizing

	Content of elements (wt%)								
	Al	Si	P	S	Cr	Mn	Cu	Zn	Fe
Electrochemical tests	-	0.09	0.01	0.01	0.04	0.32	0.08	0.03	Bal.
Bond-strength tests	0.06	0.05	0.01	0.01	0.06	0.81	0.11	0.03	Bal.

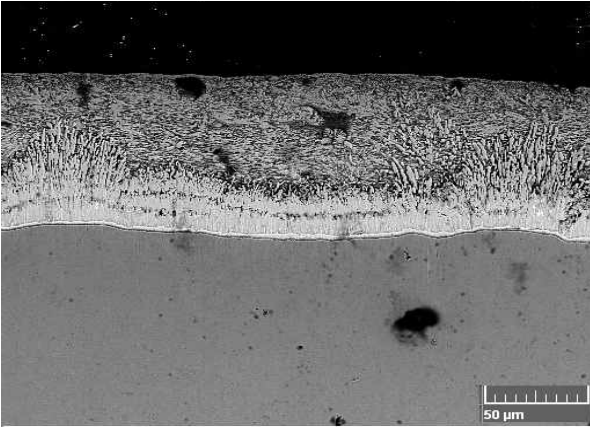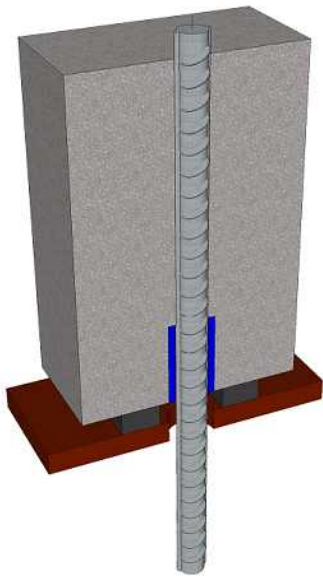Fig. 1 Structure of the coating at the hot-dip galvanized steel specimen.

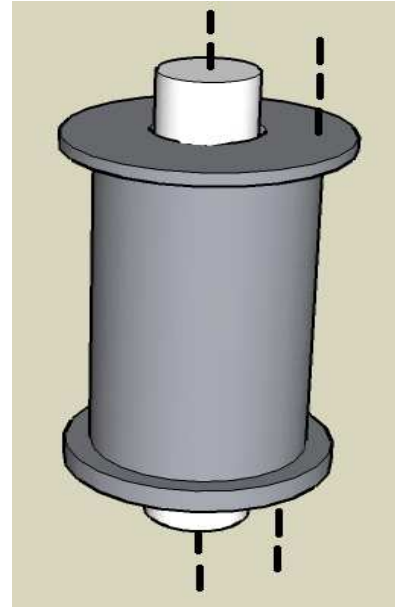Fig. 3 Schematic drawing of the modified pull-out test.
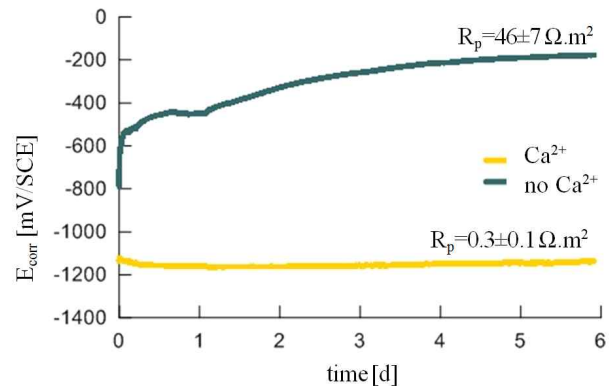

Fig. 2 Schematic drawing of the standard pull-out test.

Fig. 4 E_{corr} in dependence on time for zinc in a solution of pH 12.6 containing or not containing calcium ions.

mel reference electrode (SCE). Glow discharge - optical emission spectroscopy was used in order to describe an elemental concentration profile across the zinc coating and corrosion products.

The bond-strength of galvanized steel and carbon steel with concrete was tested by means of the pull-out test following the ČSN 73 1328 (Fig. 2). In this test, the metallic bar is being drawn out of a concrete cube after 28 days of curing in water. The bond-strength was evaluated as a stress applied to displace the bar by 0.001 mm as well as maximal applied stress for total detachment of the bar

from concrete, i.e. ultimate shear strength. The bond-strength test was modified also for zinc cast rods (Fig. 3), when the metallic rod is being pushed away from the concrete cylinder. The mentioned modification lies in more precise positioning of the rod in the axis of the cylinder so that there is just the adhesion that affects the bond-strength to concrete. Only the ultimate shear strength was evaluated in this case. The porosity of the cement binder at the concrete-metal interface was evaluated by means the surface analysis of SEM image using the Image J technique. Pores with diameter bigger than 15 μm were
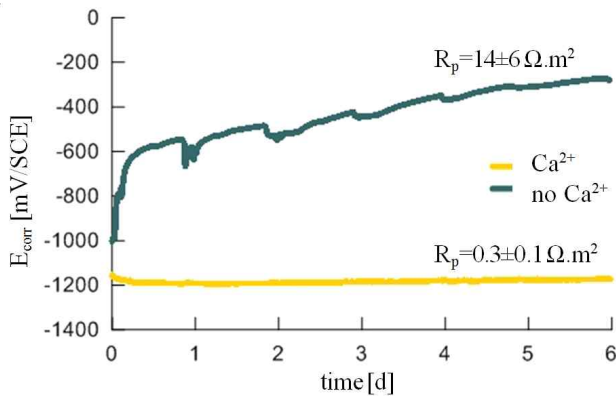
Fig. 5 E_{corr} **in dependence on time for zinc in a solution of pH 13.0 containing or not containing calcium ions.**
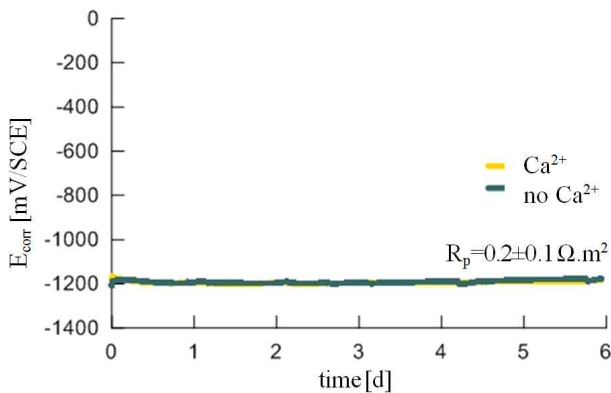

Fig. 6 E_{corr} **in dependence on time for zinc in a solution of pH 13.5 containing or not containing calcium ions.**

considered. The standard pull-out test was performed using C 45/55 grade concrete while for the modified test, commercial C 16/20 grade concrete was used after 4 months of curing at humid air (relative humidity 95 %).

3. Resutls and Discussion

3.1 Zinc corrosion as a function of pH

E_{corr} record that is identical for all the four parallel specimens exposed to KOH solution of pH 12.6 confirms immediate transition of zinc into passive state right after start of exposure (Fig. 4– green curve). High polarization resistance values in order of tens of Wm^2 at the end of exposure reveal low corrosion rate in passivity. Considering E_{corr} throughout the whole exposure period, hydrogen gas was not formed in pH 12.6 KOH solution.

Elevation of pH to 13.0 led to a slight decrease of E_{corr} having no impact on passivity of pure zinc (Fig. 5). Corrosion rate was somewhat higher (lower R_p) when compared to pH 12.6 but still the polarization resistance remained in the range of tens of $W \cdot m^2$. Neither in pH13.0

solutions, is E_{corr} not negative enough to predicate formation of hydrogen gas.

The crucial change of zinc corrosion behaviour occurred when pH of the KOH solution had been elevated to 13.5. E_{corr} remains down at -1200 mV/SCE throughout the entire exposure period (Fig. 6), i.e. in the range of water reduction to hydrogen as the dominant cathodic reaction. Zinc dissolved in active state and passivation was not observed within the 6 day exposure period. The polarization resistance dropped down to the tenths of $\Omega.m^2$.

Observed corrosion behaviour in KOH solutions with various pHs corresponds to published data in fact [2], except the transition of zinc into passivity after four days of exposure at pH 13.0.

The main finding of the results above is that corrosion resistance of pure zinc as well as of galvanized steel is very similar in model pore solutions containing no calcium ions, i.e. in environment that approximates real conditions only considering the pH level.

3.2 Zinc corrosion at presence of calcium cathions

Applicability of galvanized steel as concrete reinforcement is often approved by ability of zinc to passivate in concrete environment where of calcium ions must be expected at content corresponding to solubility of calcareous components. Nevertheless the calcium cathions have crucial negative impact on corrosion resistance of zinc in alkaline environment, as follows.

While in KOH solution of pH 12.6 zinc spontaneously passivates at the beginning of exposure, in the saturated $Ca(OH)_2$ of the same pH value zinc corrodes in active state throughout the 6 days exposure period (Fig. 4 – yellow curve). At such pH level, the calcium ions do not contribute to formation calcium zincate passive layer, contrary to that calcium ions probably reduce stability of ZnO or $Zn(OH)_2$ that leads to active corrosion of zinc with hydrogen evolution. Polarization resistance values prove the by two orders of magnitude higher corrosion rate. Further increase of pH naturally does not improve corrosion resistance of pure zinc in saturated calcium hydroxide solution. E_{corr} at the level of 1200 mV/SCE (Fig. 5 and Fig. 6) and polarization resistance prove active corrosion of pure zinc that is accompanied with hydrogen gas evolution for all the six days of exposure.

3.3 Galvanized steel corrosion at presence of calcium cathions

Like in the case of pure zinc, corrosion of galvanized steel is negatively affected by calcium cathions in pH 12.6 solution (saturated calcium hydroxide solution) that is evident from low value of E_{corr} within two days of exposure
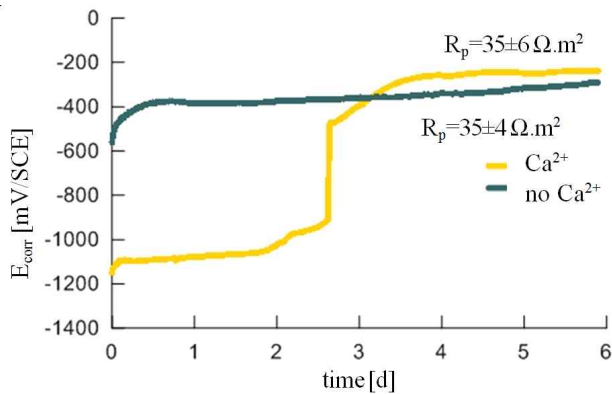
Fig. 7 E_{corr} in dependence on time for galvanized steel in a solution of pH 12.6 containing or not containing calcium ions.
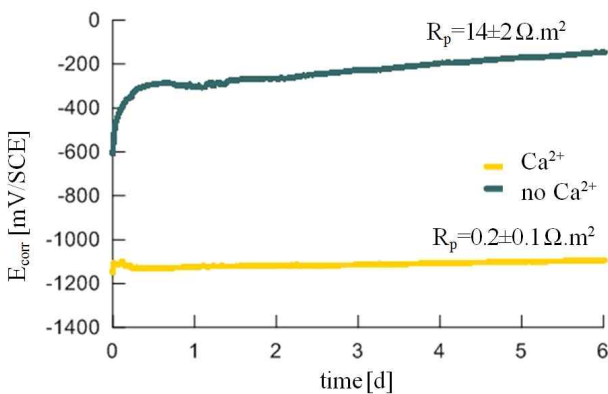

Fig. 9 E_{corr} in dependence on time for galvanized steel in a solution of pH 13.5 containing or not containing calcium ions.

Fig. 8 E_{corr} in dependence on time for galvanized steel in a solution of pH 13.0 containing or not containing calcium ions.

Fig. 10 Surface profile analysis of the galvanized steel after exposure in model solutions.

(Fig. 7). Later, E_{corr} increases to the level, which corresponds to passive state, i.e. to the level which was observed for zinc in solution of the same pH but free of calcium cathions. Values of polarization resistance also confirm the transition to passivity. It's clear then that there is evident difference in behaviour galvanized steel and zinc in saturated calcium hydroxide solution (pH 12.6) which can be explained in the case of galvanized steel in first days of exposure by dissolution of a thin topmost layer of zinc followed by passivation of one of the Fe-Zn intermetallic phase interlayer. In such a case, the appropriate Fe-Zn phase might be utilized in order to eliminate formation of hydrogen gas at zinc surface in fresh concrete. However, the realistic values of pH (>13.0) lead to active corrosion within the entire exposure (Fig. 8, Fig. 9).

3.4 Elemental profile analysis

The galvanized steel specimens were submitted to the elemental profile analysis Fig. 10. It is impossible to determine neither the concentration of individual elements no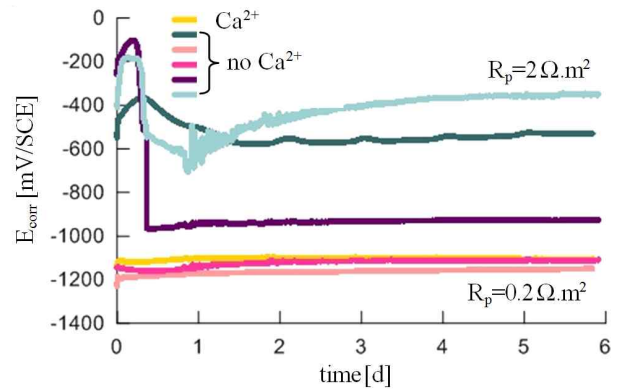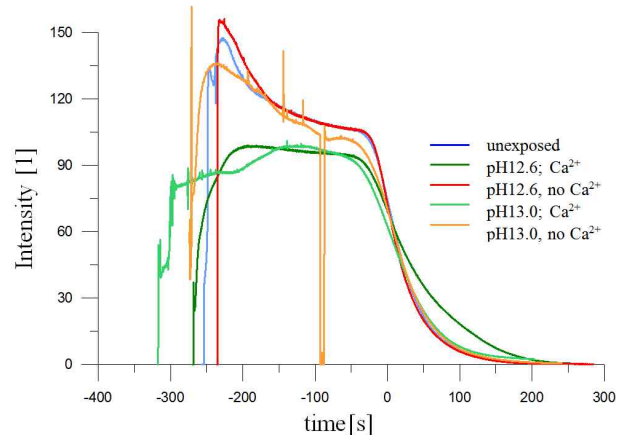r their ratio at various distances nor the thickness of remaining coating or corrosion products. Assuming equal sputtering rate for all the specimens, it is only possible to compare the remaining thickness and elemental content. Since formation of the insoluble corrosion products and consumption of the coating unequally change the thickness of the layer on the steel core of a specimen, it is necessary to compare the results by utilizing selected concentration point that is common for all the specimens.

A cross-section of the decreasing intensity of zinc signal and increasing intensity for iron was selected for such a reference point. Negative time on thus corresponds to the time needed to sputter the corrosion product layer and remaining metal to the depth of the above mentioned cross-section which was related to the time of 0.

The profiles at Fig. 10 show that the zinc coating thickness in the KOH solution of pH 12.6 (red) did not changed compared to unexposed galvanized steel specimen (blue). The signal intensity is high and same for both the specimens that probably confirms presence of pure zinc at the surface of the coating. When calcium cathions are present
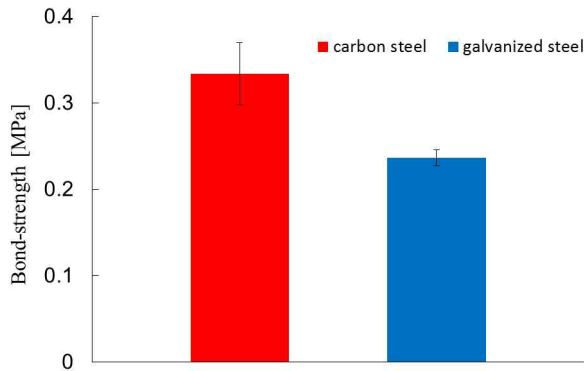
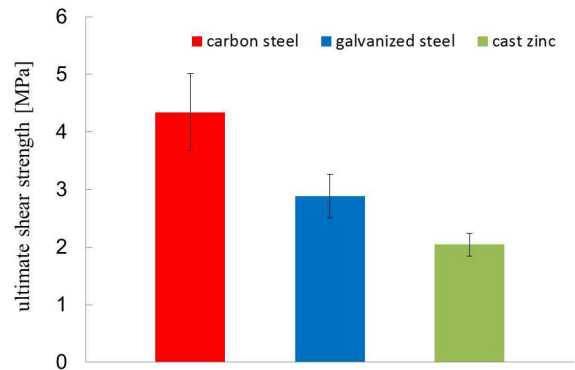**Fig. 11 Bond-strength (at 0.001 displacement) of plain bars after 28 days of curing in water.**

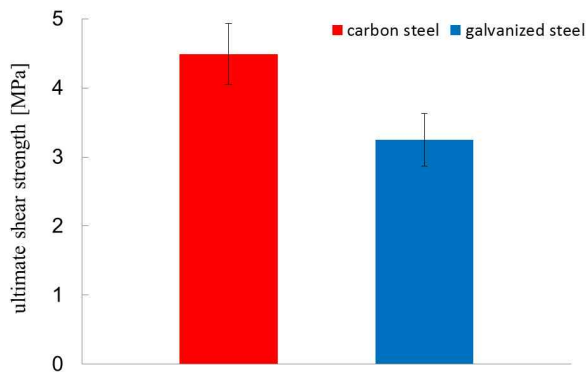**Fig. 13 Ultimate shear strength of plain rods after 4 months of curing in humid air.**

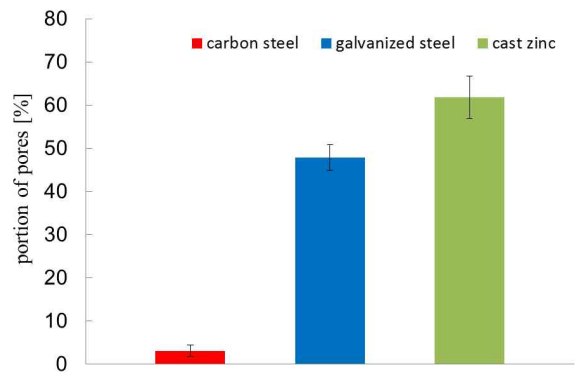**Fig. 12 Ultimate shear strength of plain bars after 28 days of curing in water.**

Fig. 14 Portion of pores at the concrete-metal interface after 4 months of curing in humid air.

(saturated $Ca(OH)_2$ solution, pH 12.6), which led to active corrosion of zinc within first two days of exposure, zinc content decreases and the content maximum moves in positive direction towards 0, i.e. the coating's thickness decreased. The transition of galvanized steel to passivity probably occurs after dissolution of the superficial zinc layer and one of the following Fe-Zn layers passivates. The transition of galvanized steel to passivity was observed in calcium free solution (pH 13.0). However, corrosion rate in passivity was higher. Slight decrease of zinc concentration (Fig. 10 – orange curve) thus probably corresponds to partial consumption of zinc layer at the surface and shift of the maximal intensity in negative direction probably because of formation of detectable corrosion products.

3.5 Bond-strength tests

Using just the plain carbon steel and hot-dip galvanized steel bars, the standard pull-out adhesion test results in clear conclusion that the bond-strength of the galvanized steel to concrete is by app. 25% lower compared to the carbon steel bond-strength (Fig. 11, Fig. 12). Longer cur-

ing time (4 months) did not change significantly the difference between the adhesion of the two materials to concrete (Fig. 13). The absolute values should not be compared because of different techniques being used and different concrete quality.

Fig. 13 clearly shows that the adhesion of a cast zinc rod is even lower than the galvanized steel rod, which might be explained by greater availability of pure zinc for corrosion in fresh concrete in the case of the cast zinc rod and thus bigger amount of hydrogen gas being formed. Such a conclusion is confirmed by Fig. 14. The cement binder at the rod-concrete interface is much more porous in the case of galvanized steel compared to the carbon steel, and even more porous in the case of cast zinc rod.

4. Conclusions

Corrosion resistance of zinc in alkaline environment depends not just on pH level but also on presence of calcium ions. Corrosion resistance is significantly reduced in model concrete pore solutions that are based on saturated calcium hydroxide compared to solutions of the same pH

but containing no calcium cathions. Pure zinc corroded even at the lowest pH level (12.6) in saturated $Ca(OH)_2$ solution meaing that pure zinc was under active state for all the exposure time with evolution of hydrogen gas. Compared to that, galvanized steel got passivated after dissolution of the surface zinc layer. Prospective higher corrosion resistance of one of the Fe-Zn interlayers is not utilizable for corrosion protection and hydrogen elimination because of its rapid corrosion at realistic levels of pH (13.0 and 13.5). The importance of amount of present pure zinc was confirmed by the bond-strength tests. Though ultimate shear strength was substantially higher for cast zinc than for galvanized steel, the bond-strength of galvanized steel and cast zinc was low compared to carbon steel. The lower bond strength was explained by the higher porosity at the interfacial cement binder.

Acknowledgments

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