

# THE INFLUENCE OF CORROSION OF ZINC POWDER ON MECHANICAL PROPERTIES OF CONCRETE

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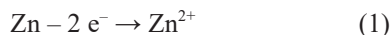
**Keywords:** Corrosion of steel in concrete, Hot-dip galvanized reinforcement, Zinc, Heat of hydration, Compression strength, Modulus of elasticity

*This paper studies the effect of zinc corrosion in fresh concrete on the process of its hydration and evolution of common mechanical properties. Process of hydration was monitored by temperature measurement of hydrating concrete contaminated with zinc powder (0.5; 5.0 wt. %) in closed system. Mechanical properties were monitored in similarly contaminated concrete samples (compressive cubic strength, compression modulus of elasticity). The results suggest that zinc corrosion products retard the concrete hydration and evolution of mechanical properties, however, forming hydrogen also has some negative effect.*

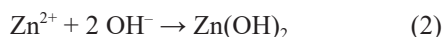
## INTRODUCTION

Utilization of hot-dip galvanized zinc coating as a means of anti-corrosion protection of carbon steel concrete reinforcement can be one of many measures to enhance the lifetime of concrete steel construction. Application of this surface treatment enhances the resistance of construction against carbonation, however its resistance of the coating against chloride anions is in question, and even more so is the effect of zinc coating on bond-strength between concrete and the reinforcement [1, 2, 3].

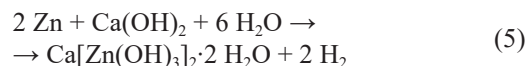
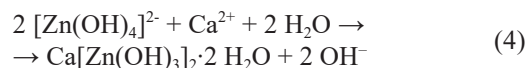
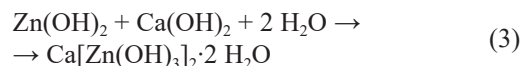
After the hot-dip galvanized steel is set into concrete, the initial corrosion reaction – anodic dissolution of zinc takes place, producing  $\text{Zn}^{2+}$  (Equation 1):



In strongly alkaline environment, the zinc cation transforms to zinc hydroxide (Equation 2):



Zinc hydroxide ( $\epsilon$  – modification) together with  $\text{ZnO}$  constitute the minor part of corrosion products on zinc or hot-dip galvanized steel [4, 5, 6]. Major component in alkaline environment in presence of  $\text{Ca}(\text{OH})_2$  is  $\text{Ca}[\text{Zn}(\text{OH})_3]_2 \cdot 2 \text{H}_2\text{O}$ . This dihydrate of calcium zincate (more precisely calcium bis(trihydroxydizincate) dihydrate) forms preferentially if the pH of model pore solution is above 12.6 (some sources state the threshold to be 12.8) [7-10]. Reaction of formation of this compound can be described as follows (Equations 3-5) [1, 4, 7, 8].



Transition of hot-dip galvanized steel from active to passive steel is typically explained by formation of crystalline  $\text{Ca}[\text{Zn}(\text{OH})_3]_2 \cdot 2 \text{H}_2\text{O}$ . It has been stated by several authors that up to pH 13.3 of the model pore solution, the surface becomes passive by the formation of the zincate [11-14]. However, there are also works with data contradicting this conclusion, explaining the transition to passive state is caused by  $\text{ZnO}$  and  $\epsilon\text{-Zn}(\text{OH})_2$  [15, 16, 17].

It has not yet been explained in detail whether this phase on the surface of hot-dip galvanized steel has positive or negative effect on its bond strength with concrete [1, 2]. According to the free corrosion potential ( $E_{\text{corr}}$ ) data, the product of cathodic corrosion process is hydrogen (6); the potential is within the range of hydrogen stability in potential-pH diagram [18]



Effect of spontaneous hydrogen evolution on the surface of hot-dip galvanized steel or pure zinc has unambiguously negative effect on porosity of cement on phase interface [2]. Filling of these pores by zinc corrosion products is nowadays questioned [19-23].

It has been mentioned before that zinc and ZnO can slow down cement curing by formation of  $\text{Zn}(\text{OH})_2$  and/or  $[\text{Zn}(\text{OH})_4]^{2-}$ . This phenomenon is commonly explained by encasing the unreacted grains of cement by these compounds, thus slowing down the hydration [24–27]. However, it has been also shown that zinc corrosion products are partially able to integrate with forming C-S-H gel and change its morphology to fibrous. It is also claimed that this phenomenon can, after 28 days, lead to enhancement of mechanical properties of contaminated concrete [28, 29, 30].

This paper is focused on effect of addition of high-purity zinc on evolution of mechanical properties (compressive cubic strength, static modulus of elasticity in compression) prepared solely from pure Portland cement. The effect of pure zinc addition on hydration heat was also studied.

Acquired data are discussed in broad context to evaluate the feasibility of hot-dip galvanized concrete reinforcement.

## EXPERIMENTAL

Pure Portland cement CEM I was used to evaluate the effect of corrosion of zinc powder (analytical purity SIGMA – ALDRICH) on evolution of mechanical properties during cement curing. Cement composition is specified in Table 1; the content of specific oxides was measured by XRF. Since the corrosion behavior of zinc in fresh concrete can be affected by chloride anions ( $\text{Cl}^-$ ) and chromate anions ( $\text{CrO}_4^{2-}$ ), the composition was further verified by ICP – OS method.

Composition of concrete mixture is summed up in Table 2.

Prepared concrete mixtures were classified as C30/37 strength category and water coefficient (w/c) was 0.57.

Table 1. Chemical analysis of the cement (XRF/ICP-OS), wt. %.

CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	SO <sub>3</sub>
56.1	27.3	4.9	3.4	2.4
MgO	Na <sub>2</sub> O	K <sub>2</sub> O	Cl <sup>-</sup>	CrO <sub>4</sub> <sup>2-</sup>
3.5	0.2	0.5	0.048	$1 \times 10^{-3}$

Table 2. Composition of concrete mixture samples (kg·m<sup>-3</sup>)

Concrete composition	Amount (kg)
Cement (CEM I – 42,5 R)	350
Aggregate – 1 (0/4 Dobříň)	900
Aggregate – 2 (4/8 Dobříň)	585
Aggregate – 3 (8/16 Dobříň)	285
Water	200

Hydration process and evolution of mechanical properties (compressive cubic strength; static modulus of elasticity in compression) of pure concrete was compared with samples contaminated with zinc powder (0.5 wt. % Zn and 5.0 wt. % Zn (relative to dry cement mass)).

The hydration process was monitored by modified test – instead of conventional hydration heat, temperature was measured. Test composed of a thermocouple enclosed in the middle of cubic mould ( $a_c = 300$  mm), fixed inside larger cube. The space between the two was insulated ( $a_i = 100$  mm) by polystyrene layer (isolated system). Temperature of the inner system, composed of curing and eventually hardening concrete, was measured in 5 minute for 15 days. In total, 3 samples were measured – a cube without any added zinc, and two contaminated with zinc. Average air temperature in the room where the cubes were stored was  $t_r = 17.5 \pm 1.5^\circ\text{C}$ .

Additionally, mechanical properties of concrete contaminated with zinc were realized. First, the compressive cubic strength of samples was tested. Four parallel specimen were produced for each cube ( $a_{ci} = 150$  mm), firstly non-contaminated and later contaminated with 0.5 wt. % Zn and eventually 5.0 wt. % Zn. Compressive cubic strength was measured on INSTRON 3000 kN device.

After comparison measurement of compressive cubic strength, the static modulus of elasticity in compression was evaluated. Four samples (bars:  $100 \times 100 \times 400$  mm) were used in each test. The properties were measured along the longitudinal axis. The loading was cyclic in range of 0.5 MPa to 1/3 of measured compressive cubic strength. Relative strain of concrete was measured during loading. Experimental device was the same as in the previous experiment. Compressive modulus of elasticity was calculated from the loading curve (stress – strain diagram).

## RESULTS AND DISCUSSION

Recorded temperatures during hydration of concrete is summed up in Figure 1. It is apparent that addition of 0.5 wt. % does not yet have effect on hydration. Slight elevation of temperature in the case of less-contaminated concrete sample relative to sample without zinc addition is caused only by zinc dissolution and formation of corrosion products (see the Introduction), because zinc dissolution in alkaline environment is an exothermic reaction.

On the opposite, higher addition of zinc powder (5.0 wt. %) to the mixture clearly retards hydration process.

Relatively mild increase of temperature of concrete sample with high zinc addition is probably caused only by corrosion of zinc powder which is accompanied by hydrogen evolution in the whole sample. It needs to be

emphasized that hydration is evidently not hindered just by corrosion products of zinc in alkaline environment in presence of calcium cations but also by the gaseous hydrogen. Forming gas displaces cement grains so far apart that they are not able to interact. Concrete samples contaminated with 5.0 wt. % zinc are much larger in volume compared to non-contaminated samples. This is apparent from Figure 2 and Figure 3. Moreover, these samples have high degree of very atypical porosity (see Figure 4).

Imperfect hydration of zinc contaminated concrete facilitates evident deterioration of mechanical properties of concrete.

Figure 5 shows compressive cubic strength data (the average of 4 measurements) after 28 days of concrete curing. It is apparent from the figure that addition of 0.5 wt. % Zn slightly reduces cubic strength. Addition of 5.0 wt. % of zinc reduces the compressive strength by up to a factor of 10. Similarly, the elastic modulus of concrete with 5.0 wt. % zinc addition is reduced about 25 %. Addition of 0.5 wt. % had no effect on value of elastic modulus (see Figure 6).

This work reasserts previous results suggesting that corrosion products of zinc in the fresh concrete have negative effect on hydration and thus also on mechanical properties evolution of mature concrete. Contamination of concrete with even small amounts of zinc does not significantly change the process of hydration and mechanical properties. The speculation can be thus drawn that reduced bond strength between concrete and hot-dip galvanized reinforcement is caused primarily by hydrogen evolution which clearly increases porosity of cement on phase interface of hot-dip galvanized reinforcement/concrete. It is also necessary to highlight that the concrete-reinforcement bond strength can be negatively affected by not only the hydrogen evolution but also formation of voluminous corrosion products from  $\text{Ca}[\text{Zn}(\text{OH})_3]_2 \cdot 2\text{H}_2\text{O}$  or  $\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$  (in uncontaminated concrete) or, e.g.  $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$  (concrete contaminated by chlorides).

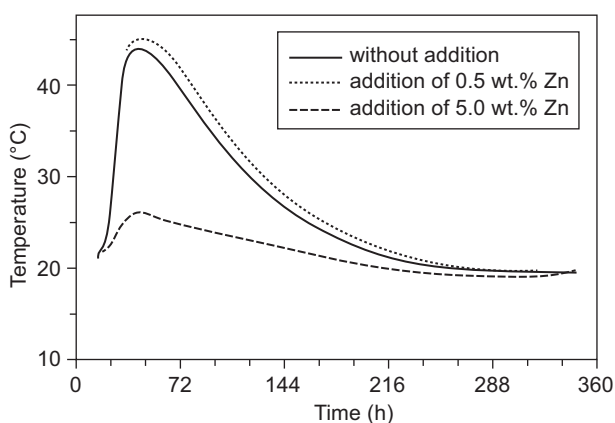


Figure 1. Hydration temperatures of hydrating concrete samples without addition or with a addition of zinc powder.



Figure 2. Appearance of “gass-filled” concrete sample with addition of 5.0 wt. % Zn.



Figure 3. Another image of “gass-filled” concrete cubic sample with addition of 5.0 wt. % Zn.



Figure 4. Detail depicting dramatic increase of porosity in sample of concrete with 5.0 wt. % addition Zn.



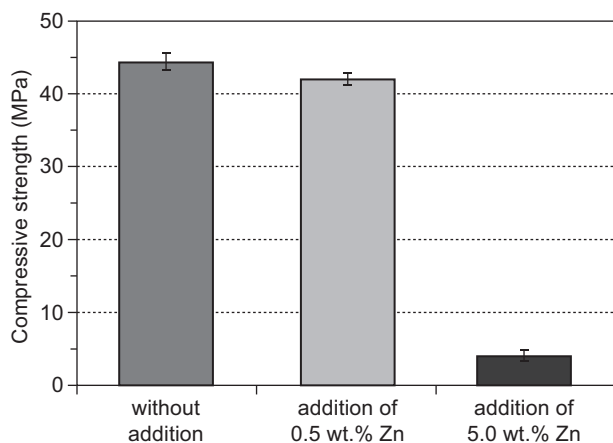


Figure 5. Comparison of compressive cubic strength of samples with different levels of zinc powder content.

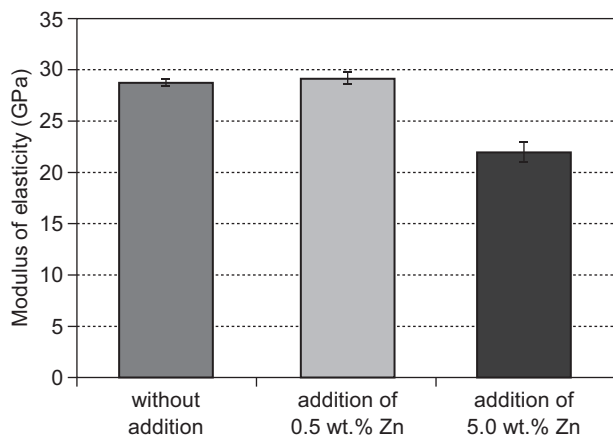


Figure 6. Comparison of compressive coefficient of elasticity of samples with different levels of zinc content.

## CONCLUSIONS

This work clearly shows that corrosion of zinc retard the process of hydration of common concrete and thus also the evolution of their mechanical properties. It is important to mention that the hydration process and mechanical properties evolution are also affected by gaseous hydrogen. Its formation causes displacement of concrete grains thus preventing their interaction.

Lower amount of zinc in concrete (0.5 wt. % in this case) has no significant effect on hydration and hence no effect on mechanical properties evolution. It can be assumed that the main factor is the increased porosity caused by forming hydrogen which facilitates the reduced bond strength between hot-dip galvanized reinforcement and concrete.

Retardation of mechanical properties of cement on hot-dip galvanized reinforcement/cement (ITZ) by zinc corrosion products has probably only minor effect on their bond strength.

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