



Effect of soluble inhibitors on the corrosion behaviour of galvanized steel in fresh concrete



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ABSTRACT

The effect of some soluble inhibitors on the passivation time of galvanized steel reinforcements in fresh concrete was studied in order to reduce H_2 evolution associated with the active corrosion. The investigation was performed by means of corrosion potential monitoring, scanning electron microscopy, energy-dispersive X-ray spectroscopy and X-ray diffraction analysis. The obtained results indicate that the passivation of galvanized steel in concrete containing chromates occurs in three steps with different mechanisms and that dissolved oxygen is necessary for the beginning of passivation process. Among the inhibitors studied as alternative to Cr VI, nitrite seem the most promising one, even if it is less effective than chromate. Diethanolamine and molybdate ions do not have significant effect on the passivation time of galvanized steel in fresh concrete.

1. Introduction

Galvanized steel has been successfully used for concrete reinforcement in many structures exposed to various conditions as early as the 1930s [1]. The corrosion protection given by steel galvanizing is due to some beneficial effects. Zinc-coated steel has a chloride threshold substantially higher than that of uncoated steel [2] and it is resistant to the effects of concrete carbonation [3]. Furthermore, the zinc coating not only is a barrier against corrosive agents, which delays the corrosion process, but it also provides cathodic protection of exposed steel when the coating is already damaged, working as a sacrificial anode [1,4,5].

Just after the embedding in fresh concrete, galvanized steel actively corrodes with the formation of gaseous hydrogen, which can lead to a loss of adhesion between the zinc coating and the cement paste not yet hardened [4,6,7]. After this stage, the pure zinc η -phase, present on the reinforcement surface, becomes passive due to the formation of a protective layer of calcium hydroxyzincate (CHZ) [8]; the active-passive transition of the galvanized reinforcement can be detected as an abrupt increase in corrosion potential from about -1.4 V to about -0.7 V vs SCE [4].

In order to prevent hydrogen evolution, conversion pre-treatments of the reinforcements have been studied by other authors [9–12]. The amount of hydrogen developed on galvanized steel during the embedding in concrete can be decreased also by adding to the cement matrix soluble inhibitors, which reduce the time of active corrosion [13–17]. The small amounts of soluble chromates, usually present in commercial cements, determine a strong inhibition of the zinc active corrosion

[13,16]. However, “chromate-reducers” (substances, such as ferrous sulfate or antimony salts, acting as reducing agents) are currently added to cements containing Cr VI, according to EU Directive 2003/53/EC; from 17 January 2005 this directive obliges to keep the content of soluble Cr VI in cement below the limit of 0.0002 wt% (2 ppm) on the total dry weight of the cement, due to its toxicity and carcinogenic effects.

In connection with the recent European Union policy for toxic materials and due to the interest of construction and building materials industry, in the last decade several studies were devoted to search for environmentally friendly chromium-free methods for corrosion protection of hot-dip galvanized steel reinforcements by means of pre-treatments [10–12,18]. Several papers investigate the efficiency of soluble inhibitors additions in cement admixtures on the corrosion protection of steel in concretes and mortars [19–28]. Currently, there are a limited number of papers dealing with the simultaneous use of hot-dip galvanized coating on reinforcements and soluble inhibitors in cement based admixtures [14,17,29–32]. Most of these works are dedicated to the use of nitrites [14,31,32]. The effect of the addition of inhibitors in concrete on galvanized steel corrosion was studied mainly to increase its corrosion resistance in presence of chloride contamination [14,17]. The results presented by different researchers are sometime contradictory and largely depend on the selection of materials and experimental conditions.

The aim of the present work was to investigate the effectiveness of some soluble inhibitors (chromate, hydrogen peroxide, nitrite, diethanolamine and molybdate) on the time of passivation of galvanized steel,

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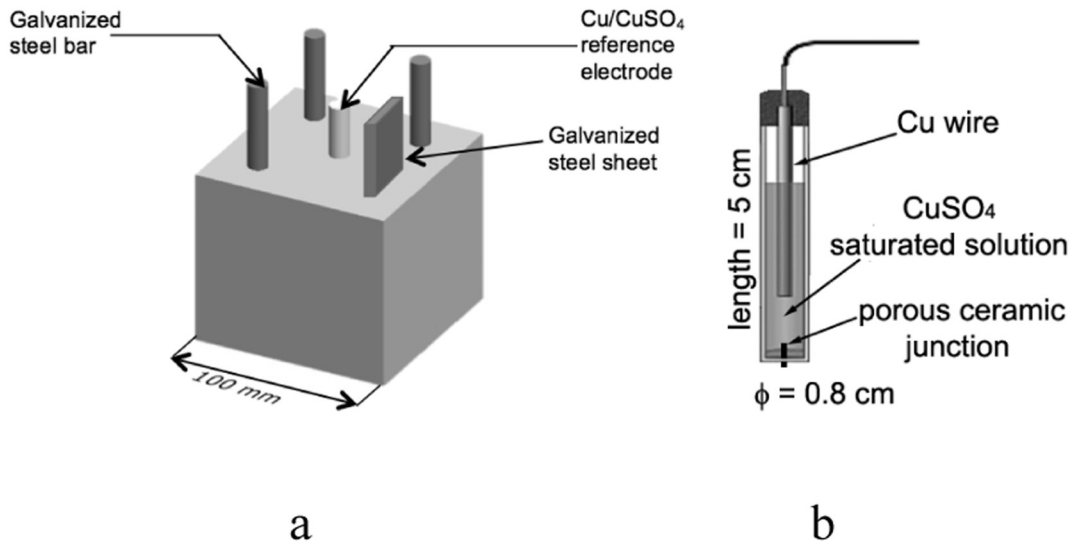


Fig. 1. Cubic concrete specimen (left) and detail of the Cu/CuSO₄ saturated reference electrode (right).

Table 1
Mix-design used for preparing 1 m³ of concrete.

Cement	420 kg
Water	230 L
Dray sand (D _{max} 6 mm)	920 kg
Dray medium aggregate (D _{max} 12 mm)	640 kg
w/c	0.6

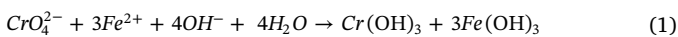
in order to find an alternative to Cr VI for reducing hydrogen evolution at the reinforcement/concrete interface. The mechanism of the effect of the studied inhibitors on the passivation of galvanized steel was compared. The study was performed by monitoring the corrosion potential of galvanized reinforcements during the early period of embedding in concrete. A grey ordinary Portland cement containing the chromate-reducer FeSO₄ and a Cr VI free white ordinary Portland cement were used. To study the effect of the inhibitors on the formation of passivating layers, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and X-ray diffraction analysis (XRD) were performed.

2. Materials and methods

Cubic concrete specimens (Fig. 1) were manufactured with the concrete mix-design reported in Table 1. Two different types of cement were used for concrete specimens preparation:

- CEM I 52.5 R, grey ordinary Portland cement (OPC) containing FeSO₄;
- CEM I 52.5 R, Cr VI-free white ordinary Portland cement (WOPC).

Grey Portland cement contains as additive the reducing agent FeSO₄, which convert water-soluble chromate into hardly soluble Cr III hydroxide:



The chemical composition of the used cements is reported in Table 2.

The inhibitors considered in this study were: potassium dichromate

Table 2
Chemical composition (wt%) of the cements used for preparing the concrete specimens.

Cement	Loss on ignition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	Insoluble residue	pH
WOPC	2.4	22.2	3.2	0.2	65.7	1.0	3.7	0.14	0.87	0.3	13.03
OPC	1.8	21.9	3.3	5.1	62.5	2.7	2.1	0.30	0.40	0.9	13.17

Table 3
Concentration of the studied inhibitors.

Inhibitors	Concentration (referred to the dry cement weight)	Concentration (mM referred to the concrete)
Cr VI	3–15 ppm	0.024–0.121
H ₂ O ₂	1.2–2.4 wt%	148–296
NO ₂ ⁻	3–6 wt%	274–548
DEA	8.3 mL/kg	36.47
MoO ₄ ²⁻	0.38 wt%	10.00

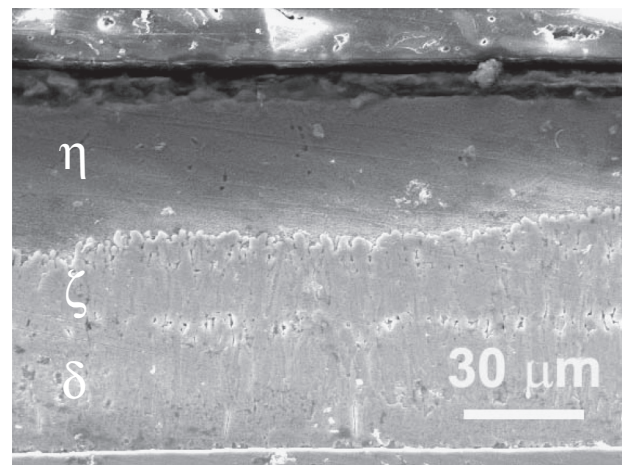


Fig. 2. SEM image of a cross-sectional area of the hot dip zinc coating.

(ACS grade, Sigma Aldrich), hydrogen peroxide (30 wt%, ISO grade, Sigma Aldrich), sodium nitrite (ACS grade, Sigma Aldrich), diethanolamine (ACS grade, Sigma Aldrich) and sodium molybdate (analytical grade, Carlo Erba). Table 3 shows the concentration of each studied inhibitor in the specimens; these concentrations were selected on the basis of literature data [14,17,33]. For comparison, some tests were

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