Influence of calcium ion in concrete pore solution on the passivation of galvanized steel bars

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ARTICLE INFO

ABSTRACT

The addition of supplementary cementitious materials may affect the Ca^{2+} concentration and pH value of the concrete pore solutions. This work studied the influence of the calcium ion on the passivation of the galvanized steel bars in simulated concrete pore solutions with relatively low pH value of 12.5 and 13.15. The results showed that continuous protective layers were formed on the galvanized coating in the solutions with saturated $Ca(OH)_2$ at pH 12.5 and solutions with either KOH or NaOH at pH 13.15. The passive film formed in the saturated $Ca(OH)_2$ solution showed better protective properties than those in other solutions. In the solutions with lower concentrations of Ca^{2+} at pH 12.5, there was no obvious reaction and no protective layer was formed on the surface.

1. Introduction

The degradation of concrete structures caused by reinforcement corrosion is a global problem and draws increasing attention all over the world. Among the corrosion preventing methods available, using galvanized steel bars is a cost-effective technique to mitigate the corrosion process and increase the service life of concrete structures exposed to aggressive environments [1–3]. The galvanized coating on the steel bars may have twofold effects [4–6]: (1) a physical barrier to the substrate carbon steel; and (2) sacrificial anodic protection to the exposed steel when the coating has been damaged or consumed, due to the less noble electrical potential. A considerable amount of studies [7–9] indicated that galvanized steel could effectively mitigate the initiation of the rebar corrosion due to the high chloride threshold value compared to the conventional carbon steel in the aggressive environment. Moreover, unlike other organically coated steel bars, galvanized steel bars are easy to be handled and transported and has high compatibility with the concrete, thus no special requirements are needed during concrete construction [2].

The passivation process of the conventional carbon steel in concrete is a spontaneous electrochemical reduction mechanism that occurs on the steel surface through interaction with the alkaline pore solution [10]. The mechanism for the galvanized steel is significantly different. Zinc, which is an amphoteric material, can vigorously react with the

high alkaline pore solution in fresh concrete accompanied by hydrogen evolution until the passive state is reached on the surface [8]. This passivation process plays a decisive role on the corrosion resistance during the initiation stage of the corrosion model of the concrete structure [2]. Andrade and coworkers [11–15] have done lots of work about the performance of galvanized steel in various alkaline solutions, indicating that pH value is an essential factor affecting the passivation of galvanized steel in concrete. The passivation mechanisms proposed were that zinc was first dissolved as $Zn(OH)_4^{2-}$ and calcium hydroxyzincate $(Ca(Zn(OH)_3)_2 \cdot 2H_2O$, CHZ) was then formed in the presence of Ca^{2+}, in which about 10 μm thickness of galvanized coating (η phase) would be consumed [4]. Hansson [5] studied the effect of the surface condition on the initial corrosion of galvanized steel in concrete, showing that the chromate film retarded the formation of the calcium hydroxyzincate, and the weathering of the galvanized coating delayed the onset of the initial corrosion. Bellezze [4,16] illustrated that oxygen is the fundamental agent for the passivation of zinc in concrete, while the concrete carbonation process can influence the products of the passive layer formed on the galvanized coating.

During the past decades, various kinds of supplementary cementitious materials [17–21], such as fly ash, silica fume and glass powder, have been used in concrete structures to reduce the cost and the CO_2 emission per ton of cementitious materials and simultaneously improve the performance of the concrete mixture. As a consequence, the pH

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value as well as the chemical composition of the concrete pore solution [22–24], especially the concentration of soluble calcium ions, may be quite different from the ones present in ordinary Portland cement. These two aspects may obviously influence the passivation of the galvanized coating on the steel bars, and the concentration of cations such as Ca^{2+}, Na^+ and K^+ may result in different corrosion products formed on the galvanized steel surface and hence affect the corrosion resistance properties. Andrade and other researchers have conducted substantial research on the passivation mechanism of the galvanized steel bars in alkaline solutions with different pH and composition. However, very little has focused on the effect of calcium ion concentration in the solutions at a certain pH level. This is of particular interest as the passivation of galvanized steel in solutions with low calcium ion concentration caused by the addition of SCMs, which has not been thoroughly studied before. This work investigated the influence of calcium ion on the passivation process of the galvanized steel in the concrete pore solutions, which aimed at revealing the passivation mechanism of the galvanized steel bars in concrete with SCMs and providing guidelines for the further investigation in the real concrete environment. To achieve this, electrochemical tests, including the open circuit potential, linear polarization resistance, electrochemical impedance spectroscopy and cyclic potentiodynamic polarization tests, were conducted to monitor the passivation process and scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction were also used to characterize the passive film.

2. Experimental program

2.1. Materials and sample preparation

The galvanized steel bars used in the present work were supplied by a local supplier in Hong Kong. They were made by S275J0 (EN 10025-2: 2004) hot rolled steel round bars which were dipped into a molten zinc bath at a temperature between 445–450 °C for about 4 min. The chemical composition of the zinc bath is given in Table 1. The specimens were cut to a dimension of Φ 10 mm × 30 mm from the produced galvanized steel bars. A copper wire was soldered to one cross section of the specimens and then the silicon was used to seal the two ends leaving an exposure surface of 5 cm². Fig. 1 illustrates the cross section of the galvanized coating, of which the thickness is about 90 μm.

The compositions of the simulated concrete pore solutions (11 types in total) are shown in Table 2. The detailed values in the table represent the concentrations of the reagents to prepare the solutions. As shown in the pore solution analyses for the cement pastes with different SCMs incorporation [22], the addition of silica fume might reduce the pH value down to the lowest value of about 12.5 and the calcium ion concentration varied in several orders of magnitude even at a pH value close to 12.5. Therefore, the solutions of pH = 12.5 were selected to simulate a relatively lower alkaline pore solution in concrete induced by adding silica fume. The dosages of the $Ca(OH)_2$ decreased from 3.5 g/L to 0 g/L for SCP 1–6 at a same pH value to represent the variation of the concrete pore solution in which the calcium ion concentration was reduced by the addition of the silica fume. SCP 1 (saturated $Ca(OH)_2$ solution) was commonly used in existing literature [25–29]. While fewer studies were conducted for SCP 2–6 with lower concentrations of $Ca(OH)_2$ or without $Ca(OH)_2$. In order to avoid the influence of the other ions, only the KOH, which is one of the main components in the concrete pore solution with SCMs [24,30,31], was selected to maintain the pH value of 12.5 in the present work. Hence,
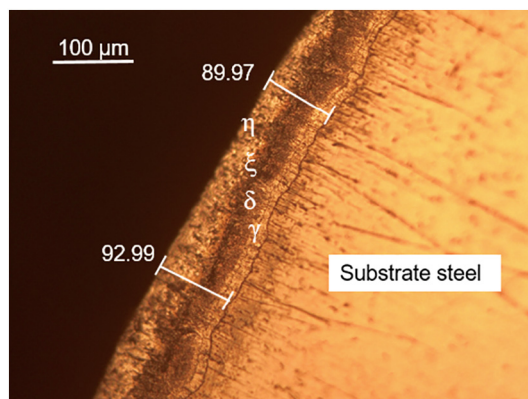
Fig. 1. Cross-section of the hot-dip galvanized steel bar observed by metalloscope. The specimen was firstly nital etched (2% nitric acid in ethanol) to reveal the four phases (η, ξ, δ and γ phase) in the galvanized coating.

Table 2
Chemical compositions of the simulated concrete pore solutions with SCMs.

Solutions	Added compounds (g/L)				pH value
	$Ca(OH)_2$[a]	NaOH	KOH	Na_2SO_4	
SCP 1	3.50	–	–	–	12.5
SCP 2	1.60	–	[b]	–	12.5
SCP 3	0.80	–	[b]	–	12.5
SCP 4	0.40	–	[b]	–	12.5
SCP 5	0.10	–	[b]	–	12.5
SCP 6	–	–	1.80	–	12.5
SCP 7	3.50	4	11.2	–	13.15
SCP 8	3.50	4	11.2	0.43	13.15
SCP 9	–	–	8	–	13.15
SCP 10	–	5.70	–	–	13.15
ECP	[c]				12.5

[a] Solubility value of the $Ca(OH)_2$ was known as 1.73 g/L at 20 °C.
[b] A proper amount was added to adjust the final pH value.
[c] Mixing water and cement by a ratio of 3:1 for 30 min without pH value adjustment.

SCP 2 - 5 were prepared by dropwise addition of the KOH solution with a high concentration into the $Ca(OH)_2$ solution. The cement extract (ECP) was made by mixing distilled water and cement (w/c = 3:1) for 30 min resulting in a final pH value of 12.5. The composition was similar to the real concrete pore solution [32], although the pH value and the ion concentration may be slightly lower. The cement used was the Green Island Portland Cement in Hong Kong (CEM I 52.5, BS EN197-1:2000) and the oxide composition is listed in Table 3.

According to the literature [30], the dominant pH values of the pore solution of CEM I with fly ash are distributed in the range of 13.0 to 13.3. Therefore, the solutions of pH = 13.15, which was also lower than the maximum pH value (13.3 ± 0.1) [33] for the zinc to form a continuous layer on its surface, was chosen to simulate the concrete pore solution with fly ash as a relatively higher pH value. SCP 7 and SCP 8 were more representative of concrete pore solutions with the main ions including Ca^{2+}, Na^+ and K^+ originated from the CaO, Na_2O and K_2O present in cement. SO_4^{2-} could be originated from the raw material of the cement or the addition of the supplementary cementitious materials [25,34,35]. Furthermore, a K^+/Na^+ mass ratio of approximately 2.8 was designed to simulate the pore solutions with fly

Table 1
Chemical composition of the zinc bath (% w/w).

Zn	Al	Bi	Cd	Cu	Fe	Ni	Pb	Sn
99.41	0.003	0.007	0.0002	0.011	0.027	0.061	0.481	< 0.002

Table 3
Oxide compositions of cement (% w/w).

MgO	Al_2O_3	SiO_2	CaO	TiO_2	Fe_2O_3	SO_3	MnO	K_2O	LOI[a]
1.47	3.77	19.37	63.85	0.26	3.08	5.38	0.06	0.69	2.14

[a] The loss on ignition was measured according to BS EN 196-1.