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Corrosion of steel reinforcement due to atmospheric pollution

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Abstract

The aim of this study is to examine the performance of four different sets of reinforcing steel rebars, S220, S400, S500s Tempcore and S500s Vanadus, exposed to the Greek atmosphere, before their installation into the concrete. The performance against atmospheric corrosion of the aforementioned steel rebars was evaluated by means of microscopy techniques and corrosion rate measurements. In particular, we studied the influence of corrosion products of a set of reinforcement steels on the bond strength between concrete and steel bars, during the hydration process of cement. Furthermore, microscopy techniques and visual observation were used to identify the rust strains and the corrosion product morphology of steel reinforcements before their installation into the concrete. The experimental results shown that the steel type, which exhibits the higher resistance, as far as atmospheric corrosion concerns, was S220 reinforcing steel. In contrary, S500s Tempcore has the least corrosion resistance. The bond strength between concrete and the steel rebars was found to decrease with increasing weathering from 45 to 122 days, due to the morphology and to the thickness of the rust layers formed on steel surface, as observed by the ESEM.

Keywords: Bond strength; Vanadium; Pre-rusted reinforcing steel; Tempcore; Atmospheric corrosion; Reinforced concrete

1. Introduction

With time and exposure to the natural environment, metals and alloys as well as the reinforcing steel rebars are converted to more stable mineral compounds. This action, which is called corrosion, changes the chemical and physical properties of the metals, frequently destroys the usefulness of construction materials or reinforced structures, and is a completely natural process. Thus corrosion has been defined as the natural reversion of a metal to an ore [1].

The degradation of reinforcing steel, due to atmospheric corrosion is of great importance for the durability of concrete structures and causes economic loss. Unfortunately in Greece, most of the times steel reinforcement is exposed to the atmosphere during transportation and storage in the building sites for a long period before their installation in the concrete structures. At any of those stages, steel rebars can be contaminated by chloride ions from sea spray or windblown salt. This fact leads to the formation of corrosion products on their surface. When these weathered steel bars are used, the presence of the corrosion products affects the bond strength between steel and concrete [2].

It well known that steel works well as a reinforcement for concrete because it bonds well with concrete. In other words, the effectiveness of the reinforcement depends on the bond strength between steel–concrete interface. The corrosion product, rust, resides at the interface between steel rebar and concrete, degrading the bond strength. On the other hand, the rougher the steel surface, the better it adheres to concrete. It has been reported that, oxidation treatment (by water immersion and ozone exposure) of rebar increases the bond strength between steel and cement paste to a value higher than that attained by clean rebars [3]. In addition, surface deformations on the rebar (such as ribs) enhance the bond due to mechanical interlocking between rebar and concrete. Literature data relating to the problem of pre-rusted steel on bond were not definite. Therefore, the effect of pre-rusted/oxidized steel rebars on bond strength quality deserves evaluation. This evaluation constitutes the main objective of this paper.

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Furthermore, this paper provides a study of four different type of steel rebars against atmospheric corrosion.

According to the Greek standards ELOT 959, 971, of steel reinforcement technology, four categories of steel rebars S220, S400 or S400s, S500 or S500s Tempcore and Vanadus based on their yield point have been defined. Each item of those categories has yielded point 220, 400 and 500 MPa, respectively. The mark "s" implies that steel reinforcement rebars can be welding. S220 steel rebar virtually can be welded, the rest of the other types can be welded under special circumstances [4,5].

Tempcore is a patented mill process that produces high-strength reinforcing rebars via inline quenching and self-tempering. The Tempcore process consists of three stages. The first stage is quenching with water of the hot-rolled steel. At the end of this operation, the rebars have an austenite core surrounded by a layer composed of a mixture of austenite and martensite. The duration of this stage depends on the required thickness of martensitic layer. In the second stage, the rebars are exposed to air. The core reheats the quenched surface layer by conduction. As a result, the martensite formed during the first stage is subjected to self-tempering. Finally, the third stage occurs as the rebars lies on the cooling bed. It consists of a quasi-isothermal transformation of the remaining austenite. The product of the conversion is a mixture of ferrite, perlite and bainite, depending on the steel composition, bar diameter, quenching duration and efficiency. As a consequence, the metallurgical microstructure and the residual stresses, which develop during the Tempcore process, contribute to superior fatigue and tensile strength properties. However, due to the differences in the microstructure across the cross section, Tempcore reinforcing steel can be treated as a composite rebar, thus its corrosion behavior must be taken into account. In contrary to Tempcore, Vanadus reinforcing steel rebars develop high mechanical properties due to chemical composition of its alloy [6–8].

S220 and S400s type of reinforcing steel rebars produces at elevated temperatures concern classical hot-rolled and cold-worked steels. The surface of S220 is completely smooth in contrary to the rest reinforcing steel types which appeared neurosis on their surface. Moreover S220 plain bars are used in concrete for special purposes, such as dowels at expansion joints and for column spirals. During the last decade in several European countries, these types of steel have been progressively abandoned and replaced by quenched and self-tempered steel [9].

The experimental method used to assess the condition of the steel rebars included weight loss throughout the experimental period. Measurements of the bond strength between concrete and steel rebars were performed in order to investigate the effects of the corrosion products on steel surface. Additionally, visual observation and microscopy techniques were used to identify the rust strains and the corrosion product morphology of steel reinforcements before their installation into the concrete.

2. Materials and evaluation methods

2.1. Atmospheric exposure of steel reinforcement

Four types of steel reinforcement were evaluated in this study: S220, S400, S500s Temcore and S500s Vanadus. They are produced by the same steelworks from Athens, Greece. The main differences between these rebars are the tensile strength and their elaboration. Their chemical composition and their yield strength are given in Table 1.

The steel rebar specimens had a cylindrical shape (100 mm long and 12 mm ∅). The test specimens were exposed during three months at the Patissia corrosion station located in the Athens. Table 2 summarizes the relevant data from this station. Each steel reinforcement as sprayed daily with 3.5 wt.% sodium chloride solution in order to increase the corrosivity of the specific region and simulate the typical exposure conditions for storage areas and building sites of reinforcing steel located in coastal and urban regions.

Prior to exposure, the surface of the steel rebars was washed with water, then immersed for 15 min in strong solution of HCl (500 ml HCl, density $\rho = 1.19$ g/ml^3 in 1000 ml distilled water) with organic corrosion inhibitor (3.5 g hexamethylene tetramine in 1000 ml distilled water) washed with distilled water to eliminate traces of the corrosion inhibitor and chloride ions (according to ISO/DIS 8407). Following that, they were cleaned with alcohol and with acetone and then weighed to 0.1 mg accuracy.

After the exposure period, the corrosion rate was determined and the corrosion products and the surface morphology were analyzed with a Moritex optical fiber microscope and Philpis ESEM XL30 environmental scanning electron microscope.

2.2. Pull-out test specimens

In order to evaluate the effect of steel corrosion products at the bond strength between rebar and concrete, clean and rusted steel rebars were used in concrete specimens' construction. All the concrete pull-out specimens were $20 \times 20 \times 25$ cm prsms reinforced axially with only one central deformed rebar (∅ 20 mm nominal diameter) using the concrete mix proportions showed in Table 3.

Table 1
Chemical composition (%) and yield strength of steel reinforcements

Type of steel rebars	Chemical composition										Yield strength (MPa)
	Elements										
	C	Mn	S	P	Si	Ni	Cr	Cu	V	Mo	
S220	0.08	0.50	0.10	0.05	0.1	0.08	0.09	0.21	0.002	0.025	220
S400	0.3	0.8	0.2	0.05	0.2	0.08	0.08	0.02	0.002	0.025	400
S500s Tempcore	0.18	0.99	0.047	0.023	0.15	0.09	0.09	0.21	0.002	0.021	500
S500s Vanadus	0.22	1.24	0.044	0.032	0.28	0.10	0.10	0.52	0.075	0.028	500

The steel rebars used were Tempcore S500s type having the same chemical composition as it is given in Table 1. The corrosion treatment of the steel rebars was conducted by exposing them into the open atmosphere (see Table 2) and daily spraying with sodium chloride solution 3.5 wt.% every 24 h, for 0, 45 and 122 days prior to embedding each rebar in concrete. The degree of corrosion was measured as gravimetric loss in weight of the reinforcing steel. The loss in bond strength of oxidized rebars was based on control specimens (clean rebars). For each treatment condition (45 and 122 days of exposure), three test specimens and three control specimens (0 days of exposure) were tested.

Thereafter, the treated rebars were positioned vertically at the center in the moulds where the concrete were cast and stored at ambient conditions in the laboratory for 24 h. After being demolded, the specimens were placed in a curing room (RH > 98%, $T = 20 \pm 1.5$ °C) for 24 h and then kept 1 day in the laboratory environment to stabilize internal humidity.

Steel pull out testing was carried out according to ASTM C-234, to investigate the difference in bond stress and rebar slip behavior. The bond tests were conducted using an ENERPAC RCH-306 testing machine of 500 kN capacity under monotonic static load. The machine was connected to a data logger and the load and slip were periodically recorded.

The slip was measured using three linear variable displacement traducers (LVDTs), which were placed at the free end to directly measure the free-end slip as the rebar was loaded in tension. The data from the LVDTS were converted into digital signals and read into a personal computer. The pull out loads were determined and reported as average values.

3. Results and discussion

3.1. Metal loss measurements

Three months after the start of this experiment, the specimens were removed from the corrosion station (see Table 2) in order to measure the weight loss of steel rebars. The steel specimens were cleaned from rust according to above-mentioned procedure, the metal loss was determined and the corrosion rates were calculated using the following equation.

$$\text{Corrosion rate } (\mu\text{m/year}) = 8.76 \times 10^{7} \frac{W}{A \times T \times D} \quad (1)$$

W: metal loss/g, A: area of steel/cm^2, T: time of exposure/h, D: density of steel/g/cm^3.

The results of mass loss measurements of a set of reinforcement steels, after three months of exposure in atmospheric conditions are given in Fig. 1.

Table 2
Environmental average data of the experimental exposure period of the corrosion station

Station	Location	Climate	Temperature T (°C)	Relative humidity RH (%)	SO_2 ($\mu g/m^3$ day)	NO_x ($\mu g/m^3$ day)	CO ($\mu g/m^3$ day)
Patissia	37.98N, 23.73′E	Mediterranean	30	25	25	110	3.5

Table 3
Concrete mix proportions (kg/m^3)

OPC cement	Water	Sand	Coarse aggregate	Crushed stone
420	210	845	338	507

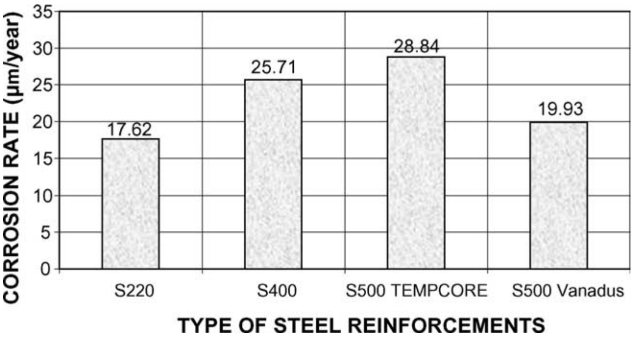


Fig. 1. Corrosion rates of S220, S400, S500 Tempcore and S500 Vanadium steel rebars, after three months of exposure at the open atmosphere.

S400 steel specimens exposed to the atmosphere for a period of three months exhibited a corrosion rate of 25.71 μm/year.

The results of the corrosion rates from the metal loss determinations are given in Fig. 1. It is observed that the steel rebar specimens, which exhibit the worst behavior against atmospheric corrosion, were S500 Tempcore.

The S500 Tempcore exhibit corrosion rate approximately 1.44 times higher than Vanadus steel rebars.

From these results, it is seemed that although Tempcore process increases the mechanical properties, makes tempcore steel more vulnerable to atmosphere corrosion.

3.2. Fiber optical microscopy observations

The fiber optical microscope used in this study was Picoscope system by Moritex.

Morphological examination of reinforcing steel types exposed to the open atmosphere showed that atmospheric corrosion begins as a localized attack on the metal surface (pitting corrosion). These points are most likely to be the sites where electrolyte is formed due to the adsorption of moisture and condensation in the presence of sulfate and chloride compounds. Upon extended exposure to the atmosphere, the localized attack gradually became a uniform form of attack covering the entire surface.

In Athens environment, the major contributors to the atmospheric corrosion process are the SO_2 and Cl^-, hot and humid conditions especially during the summer.

Salt particles containing Cl^- dissolved in the moisture layer considerably raise the conductivity of the electrolyte layer on the steel reinforcement and tend to destroy any passiviting film existing on the rebar surface. The chloride ions catalyze the liberation of Fe^{3+} and absorbs or penetrates in rust layer [10].

Some previous reports in atmospheric corrosion research referred that for salinity values of less than 100 $mg\,m^{-2}\,day^{-1}$ of chloride ions (Cl^-) there is a slight increase in steel atmospheric corrosion, which frequently increases faster with salinity values up to 400 $mg\,m^{-2}\,day^{-1}$ of Cl^- after this point the increase in corrosion with salinity again becomes slight, and then corrosion seems to stabilize as the atmospheric salinity increases [11].

After three months of exposure at the open atmosphere, the corrosion scale produced on steel rebars specimens type S220 was quite thick and the corrosion layer morphology on the steel surface was uniform. This can be observed in Fig. 2(a).

Pitting on the surface of S400 steel, S500 Tempcore rebars were observed to be the major form of corrosion (Fig. 2(b) and (c)). Briefing examination of the steel surface indicated that pits were formed under the rusted surface. It should be also noticed that S400, S500 Tempcore and Vanadus, iron oxides seem to be placed among neurons of their surface and the iron oxide layer microstructure seem to be porous (see Fig. 2(c) and (d)). On the contrary S220, exhibit substantially better performance against atmosphere corrosion.

3.3. Environmental scanning electron microscope (ESEM) observations

A Philips ESEM XL 30 environmental scanning electron microscope (ESEM), equipped with secondary

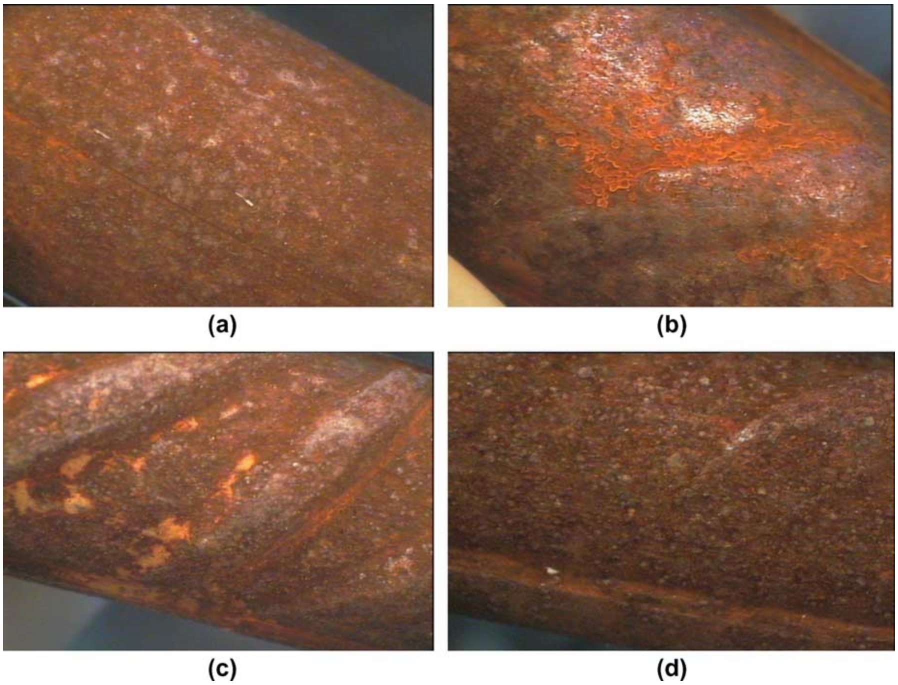

(a) (b) (c) (d)

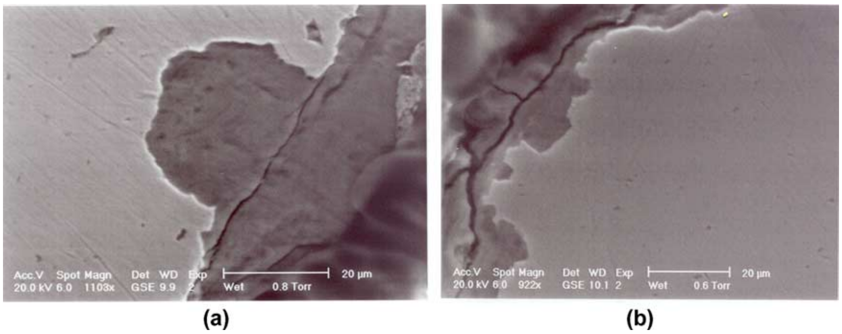
Fig. 2. Fiber optical microscope images after three months at open atmosphere conditions. (a) S220, (b) S400, (c) S500s Tempcore and (d) S500s Vanadus, steel surface morphology (×25).

and backscattered electron detectors operating at an accelerating voltage of 20 kV was used for the backscattered imaging. The ESEM was also fitted with the energy dispersive X-ray (EDX) spectrometer. The X-ray point analyses were made in specimens in S500s Tempcore and Vanadium specimens in the regions of the interface between steel and iron oxides.

In S500s Tempcore steel specimens it was possible to distinguish two different layers, in all samples, which can be called the outer and inner layer. The outer layer removed very easily from the substrate while the inner one was more adequate. It can be observed (see Fig. 3(a)) that the layer thickness morphology formed in S500s Tempcore rebar specimens, after three months of exposure to the open atmosphere in Athens, is threefold more than those that formed in the Vanadium steel specimens.

Pitting was observed to be the predominant forms of localized corrosion as revealed by backscattered electron microscopy (see Fig. 3(a) and (b)).

EDX spot analyses of corrosion products showed that blisters were enhanced in sulfur and chloride, possibly in form of iron sulfates [$FeSO_4$, $Fe(SO_4)_3$] and iron chloride, respectively. The formation of sulfate takes place simultaneously with the generation of iron chlorides. SO_2 and O_2 are initially absorbed on the surface and later converted to sulfate ions in the electrolyte with electrons provided by dissolution of iron. The reaction of negatively charged sulfate ions with ferrous ions leads to the formation of ferrous sulfate ($FeSO_4$) at anodic sites in the presence of water and oxygen, ferrous sulfate formed at anodic sites oxidizes to ferric sulfate which in turn hydrolyses to produce iron oxyhydroxide, with the generation of sulfuric acid [10].



(a) (b)

Fig. 3. Scanning electron micrograph of iron oxide morphology on (a) Tempcore S500s (×1103), (b) Vanadus S500s steel rebar surface (922×).

3.4. Bond strength tests

Regarding the question, when corroded steel is possible to be used or not, the answer depends on the thickness surface oxides. Oxides with thickness of the order of 150 μm increase the bond strength between the steel and concrete interface, due to roughness upgrade. The same does not occur though for greater oxide thickness on reinforcing steel surface [12]. According to the Fu et al., slight corrosion of steel rebars in concrete immersed in saturated $Ca(OH)_2$ solution initially increased the bond strength, while severe corrosion decreased the bond strength [13].

In the literature has been reported that steel specimens, which have been remained in calcium hydride solution for four weeks period, had exhibited greater coherence than the untreated steels. For longer periods of time through, the bond strength diminishes considerably [13]. The oxides created on the steel surface produce micro-galvanic elements which increase the corrosion rate of the reinforcing steel inside the concrete and reduce the design life of concrete structure. This can be attributed to an increase in the reactionary confinement of the rebars in the concrete, as the amount of corrosion product increases and develops an expansive mechanical pressure on the surrounding concrete. It has also been observed that for small degree of corrosion of the reinforcing rebars, significant mechanical pressure is exerted on the surrounding concrete before cracking occurs. In the initial stages of corrosion, the roughness of the rebar is also increased, thereby enhancing the friction between the rebar and the surrounding concrete. Both these effects increase the bond strength and decrease the slip of the bar [14]. Generally, In the case of reinforced concrete corrosion, the presence of chlorides in the environment produces expansive oxides that can, by cracking the concrete cover, decrease the bond strength between steel and concrete interface. On the contrary, in the case of pre-rusted steel rebars, the product formed is not expansive, rather, its fans out from the steel interface towards the concrete mass.

There are many studies on the bond strength of steel and concrete interface due to reinforcement corrosion into the concrete, but little work has been reported on the bond behavior of pre-rusted rebars in concrete. Thus the present paper reports research carried out in order to study the bond strength of pre-rusted deforms rebars in chloride environment at the steel–concrete interface. It also presents a comparison between the behavior of both pre-rusted and clean rebars.

Generally, bond strength decreases as corrosion increases. This is due to the weakening of the bond between the rebar and the concrete. Weakening of the bond is caused by the development of a less firmly adhering interstitial layer of corrosion products between the concrete and the rebars, and reduction in the rebars ribs due to pitting.

Comparisons of bond strength at different level of corrosion on steel rebars surface can be made in terms of a limiting slip or in terms of maximum load. The relationships between average bond strength and values of free end slip are shown in Fig. 4. These results clearly illustrate that bond strength decreases with the increase of corrosion rate.

The bond strength measured in pull out specimens is significantly affected by the level of pre rusted steel rebars corrosion. In particular, bond losses are increased as the thickness of corrosion products on steel surface is

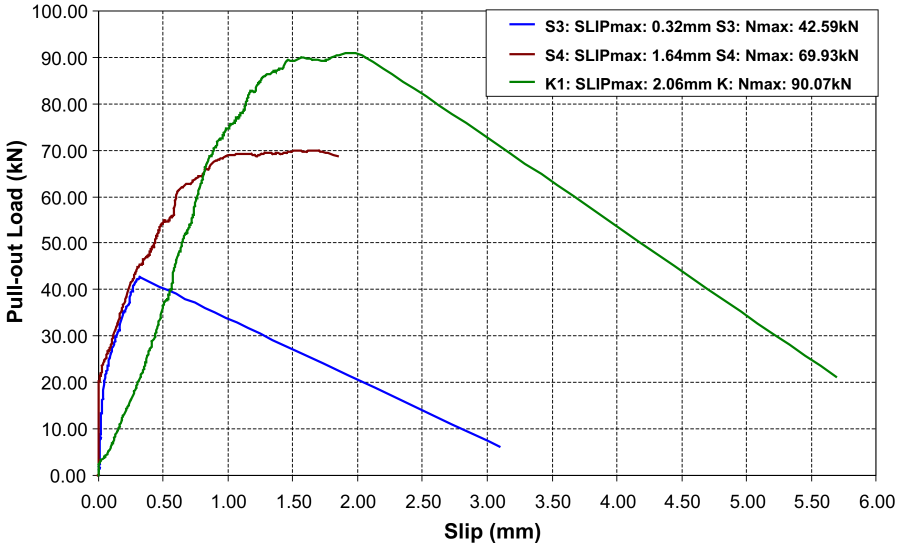


Fig. 4. Comparison of bond strength behavior vs. slip for pull out specimens with different levels of corrosion. S4: steel rebars exposed to the atmosphere for 45 days, S3: steel rebars exposed to the atmosphere for 122 days, K1: control specimens.

also increased. The adverse effect on bond is somewhat depended on the degree of initial corrosion of the reinforcements before their installation into the concrete.

Comparing the results of the pre-rusted steel rebars to those of the clean ones, the bond strength is greater in the clean ones than in the pre-rusted ones. The decrease in bond strength was substantial when the weathering of the steel rebars was increased from 45 to 122 days the bond strength between steel rebar and concrete was decreased by 22% and 53% by exposure to the open atmosphere for 45 and 122 days, respectively. This leads to the conclusion that the decrease of contact area between steel and concrete derived from the movement of iron oxides towards the concrete mass during the specimens' construction.

4. Conclusions

The experimental results have shown that S500s Tempcore steel rebars are more vulnerable in environmental conditions, compared to S500s Vanadous steel rebars.

The steel type, which exhibits the higher resistance, as far as atmospheric corrosion concerns, was S220 reinforcing steel. In contrary, S500s Tempcore has the least corrosion resistance.

Between the two S500s production methods, the better corrosion resistance was shown on the one with vanadium addition.

Steel corrosion products at great thickness were moved from the steel surface towards the inner of concrete. The iron oxides, which remained on the steel surface, have porous structure, fact that leads to the development of micro galvanic corrosion and consequently the increase of corrosion rate of the reinforced structure.

Pre-oxidized steel rebars showed significant reductions in pull-out strength, with the degradation in bond being dependent on the morphology and the thickness of corrosion products on steel reinforcements.

The bond strength between concrete and steel rebar was found to decrease with increasing weathering from 45 to 122 days, due to the morphology and the thickness of rust layer on steel surface, as indicated by the ESEM observation.

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