

# The use of inorganic conversion coatings to enhance the corrosion resistance of reinforcement and the bond strength at the rebar/concrete

M.M. Jalili<sup>a</sup>, S. Moradian<sup>a,\*</sup>, D. Hosseinpour<sup>b</sup>

<sup>a</sup> Department of Polymer and Colour Engineering, Amirkabir University of Technology, Tehran, Iran

<sup>b</sup> Department of Colour and Polymer Chemistry, University of Leeds LS2 9JT, UK

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## Abstract

The performance of concrete specimens reinforced with uncoated rebars or rebars coated with inorganic conversion coatings was investigated. The corrosion resistance of rebars and the bond strength at the rebar/concrete interface for uncoated rebars as well as rebars coated with three different inorganic conversion coatings were evaluated according to the corresponding ASTM G109 standard. The results showed that different inorganic conversion coatings give significant enhancements of corrosion resistance and increased interface bond strength compared to uncoated ordinary steel rebars. However the extent to which each conversion coating improves the corrosion resistance of the rebars and the interface bond strength inevitably depends on the chemical composition of the applied inorganic conversion coating.

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## 1. Introduction

In recent years, the corrosion of reinforcing steel rebars in concrete systems, has gained considerable attention [1,2]. Reinforcing bars having higher corrosion resistances compared to the common carbon-steel rebars can be used to provide more protection against corrosion in aggressive environmental conditions or when a long service life is required. The corrosion resistance of rebars can be increased either by modifying the chemical composition of the steel rebars or by applying a metallic or an organic coating on to the surface of such rebars. Three families of reinforced bars have commonly been used in reinforced concrete structures to protect against corrosion, namely stainless-steel, galvanized-steel and epoxy-coated rebars [1,2]. Fiber-reinforced polymer (FRP) rebars, usually

consisting of an epoxy matrix with carbon or aramide fiber, have also been proposed as a possible replacement.

However, FRP rebars are still in experimental phase and there is a lack of experience on their durability [3,4].

There are also some disadvantages associated with the main rebar types that are currently being used. For example, stainless-steel bars are much more expensive than the carbon-steel ones. Galvanized-steel rebars, in addition to being high priced due to the high price of the galvanizing process, have a further disadvantage of having an exponentially increased rate of corrosion at pH values above 13.3. Furthermore, in chloride-contaminated concrete, the galvanized-steel may be affected by pitting corrosion. Also, the reactions between metallic zinc and the hydration products may affect the bond strength between the galvanized-steel and the concrete [1,2,5]. Requirements for epoxy-coated reinforcing bars are reported in different international standards such as ASTM A775-81. Although, the price of epoxy-coated bars is higher than that of the

\* Corresponding author. Tel.: +98 2164542425; fax: +98 2188080871.  
E-mail address: [moradian@aut.ac.ir](mailto:moradian@aut.ac.ir) (S. Moradian).

uncoated bars, the main problem is the reduction of bond strength between the epoxy-coated rebars and the concrete, especially when smooth round rebars are used. Therefore design procedures have been developed to account for this influence. These include increasing the splice length by 20–50% [1,6]. The most common epoxy coating for this purpose is the fusion-bonded epoxy (FBE) that is applied as a fused powder [7,8]. Many authors have examined the cathodic delamination of FBE-coated rebars where a cathodic protection (CP) was simultaneously applied [9,10], and such delaminations have been considered as further failures of epoxy-coated rebars.

In the present paper, the performance of a phosphate conversion coating applied to steel rebars in a concrete system was evaluated. The idea of using an environmentally friendly phosphate coating to impart corrosion resistance to iron and steel surfaces goes back to at least 100 years. Nowadays, the phosphating process has been developed as a pretreatment method for painting, especially in the automotive industry, providing enhanced corrosion protection with greatly improved paint bond to the substrate. This process is now being used in car-manufacturing companies globally prior to and in conjunction with cathodic electrodeposition of car bodies. The economic importance of this process is best illustrated with reference to the automotive industry. Almost all car and van body components that are currently being made of a metal or a metallic alloy, are phosphated before painting [11]. Additionally, it must be noted, that according to the ASTM A767/A767M-90 standard specification for zinc coated (galvanized) steel bars for concrete reinforcement there are two types of coatings depending on their specified thicknesses. There are classified as Class I and Class II in which the amount of zinc used per square meter of substrate is  $>610$  and  $>1070$  g/m<sup>2</sup>, respectively giving an equivalent thicknesses of about 85  $\mu$ m and 150  $\mu$ m of zinc coated on the steel rebars, respectively. There are several methods for applying a zinc coating; hot dipping, spraying, electrodeposition and diffusion. Hot dipping is the most commonly used for producing galvanized-steel reinforced bars which is rather energy consuming (temperatures of around 450 °C).

Furthermore, the epoxy coatings are applied to the rebars, either in liquid form or in powder form. Since the permeability through the epoxy coating is lower when it is applied as a fused powder, therefore this method is commonly used for producing epoxy-coated reinforcing bars. According to the ASTM A775M/775M-93 standard specification for epoxy-coated reinforcing steel bars, the thickness of the coating is in the range of 130–300  $\mu$ m.

On the other hand the presently proposed phosphate coating only requires 10–15 g/m<sup>2</sup> of phosphate coating equivalent to thicknesses of 5–25  $\mu$ m in order to achieve optimal performances.

Since the material and processing costs are also lowest in the case of conversion coatings consequently, phosphate conversion coating is one of the cheapest coatings available [11,12a].

The objective of the present study was to investigate to what extent the application of an environmentally friendly phosphate conversion coating on a rebar would enhance the bond strength between the concrete and the rebar in addition to the increased corrosion behavior of the rebar itself.

It must be noted that many workers previously examined the bond strength between rebars and concrete bulk. For instance Kilic et al. [12b] examined the effect of bar shape on the pull-out capacity of fully-grouted rockbolts using smooth surface bars, ribbed bars, and many other bars having different shape and number of lugs.

They found out that the bond strength of the smooth surfaced rock bolt was primarily the result of the adhesion or friction that occurring at the bolt-ground interface. The bond strength of a ribbed bar on the other hand, was the result of shear strength of the grouting material. Yet, furthermore, the bond strength of a conical lugged surfaced bolt was the result of the combination of the shear and compressive strength of the grouting material. It was found, therefore, that bond strength of a ribbed bar was, on average 5.5 times greater than that of a smooth bar, and the bond strength of a conical lugged surfaced bolt was found, on average to be 27% greater than that of a ribbed bar.

These results clearly show the dependency of bond strength on many factors such as form, shape, geometry, number of lugs, etc.

Since in the present paper only the adhesion of phosphated rebars and concrete bulk was sought after, therefore smooth round, rust removed rebars were purposefully chosen to focus only on the interactions between the phosphated areas and the concrete bulk.

## 2. Experimental methods

To coat the rebar specimens, three different conversion coatings were chosen. A tri-cationic Zn–Ni–Mn phosphate Coating, with a given code of CC1 and, two, di-cationic conversion coatings based on Zn–Ni phosphate and Zn–Ca phosphate given the codes CC2 and CC3, respectively (see Table 1). (All the phosphate coating chemicals were provided by Natavest Shimie, a domestic manufacturer).

To this end, smooth and round conventional 10 mm diameter steel rebars were acid pickled in a 5% phosphoric acid solution in water at 65–70 °C for 20 min. The rebars were then rinsed in distilled water and dried by acetone. After removing metal oxides (rusts) from the rebars by acid pickling, they were immersed in three different solutions

Table 1  
Phosphate coatings' composition and code

| The phosphate material | Given code |
|------------------------|------------|
| Zn–Ni–Mn phosphate     | CC1        |
| Zn–Ni phosphate        | CC2        |
| Zn–Ca phosphate        | CC3        |

each containing 20 cc of a particular conversion coating chemical (i.e. CC1 or CC2 or CC3) in 1000 cc of distilled water. The temperature and the time of applications being 55–90 °C and 5–15 min depending on the type of phosphate chemicals as seen in Table 2. The rebars were finally rinsed with distilled water and dried at 30–35 °C.

Three rebars were selected as control after the acid pickling process, therefore no conversion coating was applied on them.

To prepare samples for bond studies, each rebar was embedded in the center of a 10 × 10 × 10 cm<sup>3</sup> cube of concrete and its bond strength was measured according to the ASTM A944 standard. Also, the corrosion resistance for the reinforced concrete systems was investigated according to the ASTM G109 standard. Potential measurements were carried out on a Hioki digital multimeter (Japan-model: 3256) and Ag/AgCl<sub>2</sub> (Autolab – Holland) was used as the reference electrode.

All of the concrete specimens prepared using a water/cement ration of 0.5 and a cement content of 400 kg/m<sup>3</sup>. The average compressive strength for the prepared concretes was 30 N/mm<sup>2</sup> after 28 days.

**3. Results and discussion**

*3.1. Bond study*

Table 3 lists the bond strength values of the phosphated and the unphosphated rebars. For each type of conversion coating, three samples were prepared as described in the experimental section, so that 8 cm of rebar length was embedded inside the concrete bulk to be above the lap length (Fig. 1). Bond strength was measured by a hydrodynamic equipment, so that the mounted concrete was fixed whilst the outer part of the rebar was connected to the driving holder.

Then the driving holder was moved and the ultimate force required to pull the rebar off was recorded (similar to ASTM A944). The results are shown in Table 3.

Fig. 2 illustrates clearly a significant increase in the bond strength between the rebar and the concrete bulk as a result of application of the conversion coatings.

The application of CC3 conversion coating on to the rebar resulted in a 74% increase in the bond strength between the rebar and the concrete compared to the bond

Table 3  
Bond strength between rebar and concrete for coated and uncoated rebars

| Sample  | Failure loads (kN)      | Average bond strength (MPa) |
|---------|-------------------------|-----------------------------|
| Control | 5.20, 5.40, 5.05        | 2.08                        |
| CC1     | 6.57, 5.20 <sup>a</sup> | 2.34                        |
| CC2     | 7.11, 6.62, 7.36        | 2.80                        |
| CC3     | 8.93, 9.81, 8.53        | 3.62                        |

<sup>a</sup> One of the sample did not have a completely vertical rebar; therefore it was ignored since it would form a horizontal force vector.

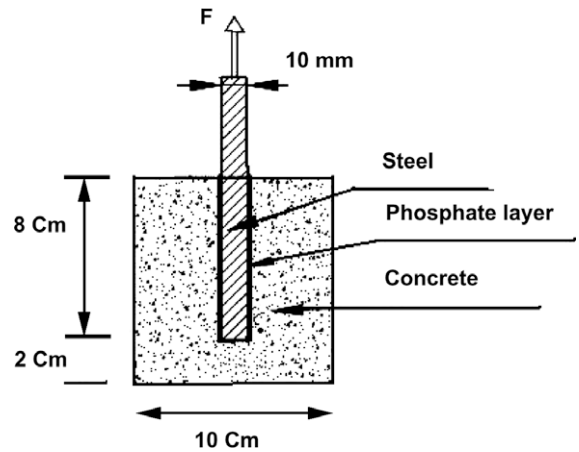


Fig. 1. Schematic scheme of prepared samples for bond studies.

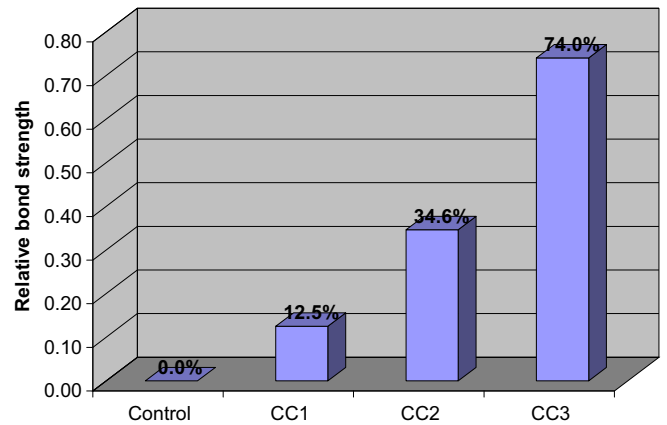


Fig. 2. Percentage increase of bond strength between the rebar and the concrete for different phosphate coated rebars compared to the bond strength between the control rebar and the concrete.

Table 2

The processing time and temperature for each conversion coating and the number of rebar samples prepared for each test

| Phosphate coating code | Bath temperature (°C) | Processing time (min) | Number of samples prepared for bond study | Number of samples prepared for corrosion study |           |                   |
|------------------------|-----------------------|-----------------------|---|--|-----------|-------------------|
|                        |                       |                       |   | ASTM G109                                      | ASTM B117 | Soaked in 5% NaOH |
| CC1                    | 55–60                 | 3–5                   | 3   | 9  | 3         | 3                 |
| CC2                    | 70–80                 | 15                    | 3   | 9  | 3         | 3                 |
| CC3                    | 75–90                 | 5–10                  | 3   | 9  | 3         | 3                 |
| Control (bare rebar)   | –                     | –                     | 3   | 9  | 3         | 3                 |

strength between the control rebar and the concrete (Fig. 2).

### 3.1.1. Bond mechanisms

A number of mechanisms have been proposed for the bond between an adhesive and an adherent (substrate) including: mechanical interlocking, adsorption, and electronic interactions [13,14].

The mechanical interlocking theory of bond states that a good level of bond would exist only when an adhesive penetrates into the pores, holes and other irregularities of the adhered surface of a substrate, and interlocks mechanically to the substrate. Formation of a conversion coating on the rebar surface provides a rough surface with a high degree of porosity. The micro-roughness created by the presence of a conversion coating on the rebar surface, can improve the bond strength between the rebar and the concrete via mechanical interlocking [14].

Some literature [1,6] have indicated that epoxy coatings would decrease the bond strength between concrete and rebar because of smooth and flat surface of the epoxy coatings. Considering the fact that epoxy coatings are organic in nature and the constituent elements of concrete are inorganic in nature, one can argue that the interaction between two materials of different natures would not be as strong as if the two materials were of the same type (e.g. inorganic). Being inorganic in type, the phosphate conversion coatings seem to be capable of stronger interactions with concrete, than epoxy coatings.

To have a better understanding of the interactions between concrete and rebar other bond theories must be reviewed. The adsorption theory includes primary (covalent) and secondary (dispersion, dipole and hydrogen) bond interactions between the adhesive (concrete) and the adherent (phosphated rebar), whereas electronic theory focuses on polar Lewis acid–base contributions. From a thermodynamics point of view, the surface free energy ( $\gamma^S$ ) can be summarized as follows [13,15,16]:

$$\gamma^S = \gamma^{LVW} + \gamma^{AB} \quad (1)$$

Here,  $\gamma^{LVW}$  is the Liftshiitz–Van der Waals (dispersive + dipole) contribution and  $\gamma^{AB}$  is the acid–base contribution.

With regard to what was mentioned earlier about the interactions between two materials of the same type, the non polar component ( $\gamma^{LVW}$ ) might increase through better penetration of the bulk concrete into the porous phosphate coating.

The second component is  $\gamma^{AB}$ . The contribution of acid–base interaction between the concrete and the phosphated rebar is, however, more significant than the non polar component ( $\gamma^{LVW}$ ) because of the considerable interaction possible between the acidic surfaced phosphate coating and that of the concrete constituents having a basic characteristic.

The coating composition is largely governed by the nature of the formed cations in the bath and the composition of metals to be phosphated [11]. Therefore, the widely different behavior of the three phosphate coatings regarding bond strength could thus be explained.

### 3.2. Corrosion studies

It was of interest to find out whether or not the incorporation of the phosphate layer could enhance the corrosion resistance of the concrete system.

All coated rebars were soaked in a 5% solution of NaOH in water for one week to simulate concrete environment in the wet-state (pH > 12). After the immersion per-

Table 4  
Salt spray resistance of coated and uncoated rebars (according to the ASTM B117)

| Sample         | Time of corrosion resistance |
|----------------|------------------------------|
| Control        | <5 min                       |
| Coated samples | Approximately 720 min (12 h) |

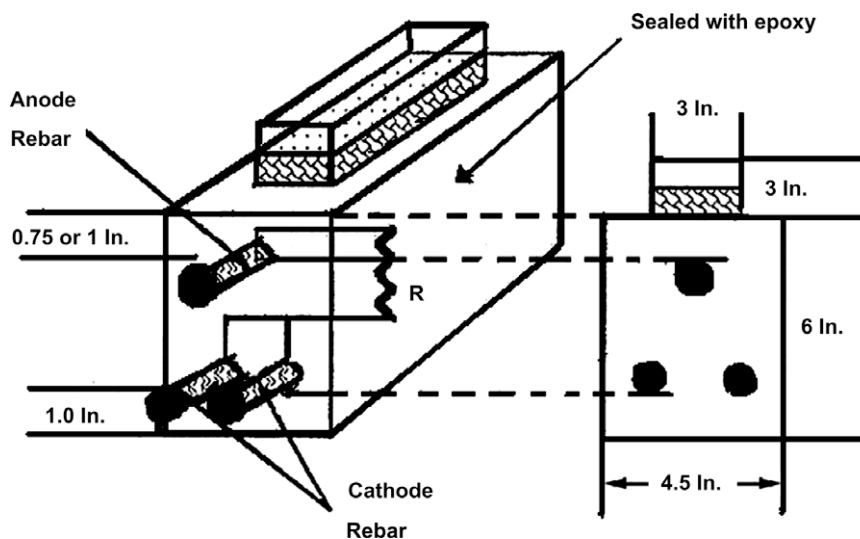


Fig. 3. Schematic scheme of prepared samples for corrosion studies according to the ASTM G109 standard.

iod, it was found that the weight losses for the rebars were less than 0.01% implying that such weight loss was negligible.

Also, coated rebars and controls were exposed to salt fog of 5% NaCl at  $40 \pm 2$  °C in a salt spray cabinet according to the ASTM B117 standard.

In such a highly corrosive condition, the control rebars rusted immediately whilst all coated rebars resisted corrosion for approximately 12 h (Table 4).

Furthermore, corrosion resistance of coated rebars was examined whilst they were embedded inside the concrete according to the ASTM G109 standard.

To prepare each sample, three rebars were used. The rebars were connected to each other by a 100  $\Omega$  resistor [17]. Fig. 3 illustrates how the concrete system was prepared for corrosion studies.

After the full curing of concrete was completed, the top container seen in Fig. 3 was filled up with a solution of 3% NaCl in water, so that the chloride ions could penetrate into the concrete bulk easily and attack the metallic rebars. For each conversion coating composition three separate samples were prepared and the average passed current was recorded at various time intervals.

Penetration of  $\text{Cl}^-$  anion through the porosities and capillary areas of concrete accelerates the corrosion reactions of the steel rebar. According to the ASTM G109 standard when the mean current exceeds 10  $\mu\text{A}$ , the electrochemical process of corrosion will start on the surface of the rebar embedded inside the concrete system.

Table 5 illustrates the mean corrosion current and potential values for the systems containing uncoated (control) and coated (i.e. with various conversion coatings) rebars. The results shown in Table 5 were recorded after 2-weeks of exposure to a solution of 3% NaCl in water followed by 2-weeks of exposure to dry conditions according to the ASTM G109 standard.

The measured current values given in Table 5 indicate that the electrochemical reactions of corrosion had started for all steel rebars inside the concrete system, except for the system in which the rebar had a CC2 conversion coating layer.

As expected the maximum corrosion current value belongs to the control sample, meaning that the system was less resistant against corrosion compared to the other systems. Therefore, of the systems studied in the paper, the uncoated control rebar is the most susceptible system to corrosion.

Table 5  
Average corrosion current and potential values for coated and uncoated rebars, after one cycle

| Sample  | Average corrosion current value ( $\mu\text{A}$ ) | Average potential value (V) |
|---------|---|-----------------------------|
| Control | 84.5  | -0.438                      |
| CC1     | 29.5  | -0.424                      |
| CC2     | 1   | -0.251                      |
| CC3     | 11  | -0.405                      |

Table 6  
Average corrosion current and potential values for coated and uncoated rebars after two cycles

| Sample  | Average corrosion current value ( $\mu\text{A}$ ) | Average potential value (V) |
|---------|---|-----------------------------|
| Control | 66  | -0.512                      |
| CC1     | 17.5  | -0.385                      |
| CC2     | 1   | -0.273                      |
| CC3     | 15.5  | -0.345                      |

The coated rebar with CC2 conversion coating, gave a corrosion current of 1  $\mu\text{A}$  which does not seem big enough to be able to start electrochemical corrosion reactions noticeably. This means that the CC2 system exhibited excellent corrosion resistance in the provided corrosive environment.

To explain the improvement in the corrosion resistance achieved through the introduction of a phosphate coating, attention should be drawn to the fact that phosphate coatings increase cathodic areas on the rebar surface resulting in a passivation and higher charge transfer resistance. Also by applying the phosphate layer on the rebar, cathodic area/anodic area ratio increases, thus the open circuit potential (OCP) increases to a maximum point. Therefore, from the potential values, given in Table 5, the system of CC2 and the control system can be considered as the most resistant system and the least resistant system respectively, against corrosion [18,19].

The cycle of 2-weeks wet and 2-weeks dry exposure periods were repeated in the subsequent month followed by measuring the corrosion current and potential values for the systems (Table 6).

By taking the current values obtained from the second cycle (Table 6), it can be noticed that again the CC2 system exhibited an excellent resistance against corrosion. By comparing Tables 5 and 6, it can be mentioned that for samples of control and CC1 the corrosion current decreased from cycle 1 to cycle 2, while for system CC3 the corrosion current increased. The decrease in the corrosion current contradicted the initial expectation that, on increasing the cycle number, the corrosion current should increase. The reason for such decrease can be attributed to the formation of corrosion products on the anodic surfaces hence decreasing the anodic areas [19,20].

At the end of three full cycles, all samples were broken and reinforced bars were examined visually. Extensive corroded area of control rebar inside the concrete system was noticed. Also, a smaller corroded area on CC1 and CC3 rebars was noticed. There was no damaged area on the CC2 rebars providing another evidence for the excellent corrosion resistance of this kind of conversion coating inside the concrete system.

#### 4. Conclusion

In this study the effect of three different conversion coatings (Zn–Ni–Mn phosphate, Zn–Ni phosphate and Zn–Ca

phosphate) applied to steel rebars on the performances of a reinforced concrete system was investigated. The performances of interest were bond strength and corrosion resistance. Bond studies were conducted using the pull-off test. The studies of corrosion resistance were performed according to the ASTM G109 standard. For the three conversion coatings studied in this article, the bond results showed that the bond strength between the rebar and the concrete increased compared to the bond strength between the control rebar and the concrete.

For the system in which the Zn–Ca phosphate had been used, the enhancement in the bond strength between the rebar and the concrete was maximum (74% increase). This enhancement can be explained by three bond mechanisms. Of the three bond mechanisms, the mechanical interlocking seems to be the dominant mechanism.

The results obtained from the corrosion studies proved that the application of a phosphate conversion coating on a rebar significantly improves the rebar's resistance to corrosion.

Minimum corrosion current and maximum corrosion potential values were obtained for the system of Zn–Ni phosphate conversion coating, implying its excellent resistance to corrosion.

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