

# The effect of using natural pozzolan-based cement concretes on zinc phosphated rebars corrosion

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**Abstract.** Studies on using zinc phosphating in reinforced concrete (RC) field are still in the early stages. Use of natural pozzolan (NP) as cement replacement is growing rapidly in the construction industry due to its economical, ecological and technical benefits. Four phosphating baths were prepared; Zn phosphate (P-Zn), Zn-Ni phosphate (P-Zn-Ni), Zn-Cu phosphate (P-Zn-Cu) and Zn-Mn phosphate (P-Zn-Mn) respectively. Ø14 mm reinforcing steel bars were treated at 55-60 °C for 15 min in the phosphating baths. Concrete specimens were produced with different levels of NP; 0% (control specimen), 10 %, 20% and 30%, respectively. The effectiveness of using both NP and P-Zn coatings in retarding rebar corrosion has been investigated using an accelerated test after 28 and 90 days concrete curing. In addition, the bond strength between the concrete and the rebar was investigated by the pull-out test. Test results revealed that the concretes containing higher replacement levels of NP and rebars treated in bi-cationic baths exhibited corrosion initiation periods several times longer than the control specimens with uncoated steel and a zero NP content. Moreover, the results showed that the bond strength was not affected by adding NP and P-Zn coatings. SEM analysis was employed, as well.

## 1. Introduction

Treatments of reinforcing steel in zinc phosphate baths could be probably a vital approach in the future [1-6]. The phosphating process was extensively used in the automobile and appliance industries [7, 8]. This treatment primarily provides an inexpensive [8, 9], non-toxic [10, 11], reasonably hard, highly adherent and electronically non-conducting phosphate coating [12]. However, the obtained phosphate coatings usually contain pores, which are pathways for the corrosive electrolyte diffusion into the metal substrate. As a result, the corrosion resistance of the conventional phosphate coating is not high enough. Additives such as  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mo}^{2+}$  and nanoparticles have been extensively used to produce phosphate coatings with uniform structure, lower porosity, higher corrosion resistance and improved adhesion properties [3-5, 8, 13-15]. A state of the art mini-review of these additives and their effects on characteristics of the zinc phosphate baths has recently been published by al-Swaidani [16].

Natural pozzolan (NP) is being widely used as cement replacement due to its ecological, economic and performance-related advantageous properties [17-22]. However, its use caused a lower alkalinity compared with plain Portland cement [23]. This could be due to the reduction in cement content (i.e.



the dilution effect) when adding natural pozzolan and the consumption of portlandit (CH) through the pozzolanic reaction.

Syria is rich in natural pozzolan with estimated reserves of about one billion tonnes [24]. Although there are numerous studies on using natural pozzolan as cement replacement, the authors think that no work has been carried out in the past to investigate the combined effect of adding NP as cement replacement and zinc phosphate coated steel on the anti-corrosion properties of reinforcing steel exposed to highly chloride ion concentrations. In addition, literature did not cover the benefit, in terms of alkaline stability, which can be achieved when the zinc phosphate coated steel is embedded in concrete of a relatively lower alkalinity. Further, the reduced concrete permeability offered by NP-based cements could be considered an additional physical barrier between steel and its environment.

The objective of this paper is to investigate the influence of adding NP as cement replacement on the corrosion performance of reinforcing steel treated in different zinc phosphate baths. Four binders with different replacement levels of NP (0, 10, 20 and 30%), have been produced for this investigation. In addition, four zinc phosphating baths were employed; the first one is a mono-cation bath (i.e. it contains only Zn-cation), and three bi-cation baths; Zn-Ni, Zn-Cu and Zn-Mn, respectively. The effect was studied in terms of corrosion resistance and the bond strength between the treated reinforcing steel and the NP-based concrete.

## 2. Experimental Procedure

Natural pozzolan (NP) used in the experiments was collected from a Tal Shihan' quarry, 70 km southeast of Damascus, Syria. More detailed information related to its characteristics can be found in the recently published research work of al-Swaidani et al. [25]. Four binder specimens have been prepared; one plain Portland cement CEM I (control) and three binary binders with three replacement levels of 10%, 20% and 30% NP (EN 197-1). 5% of gypsum was added to all the binder specimens. All replacements were made by mass of cement. All binders were designated according to the replacement level. For instance, NP10 and NP30 refers to the binders containing 10% and 30% of NP, respectively. More data on the characteristics of the binder components, namely, particle size distribution and the grinding method can also be found in the scientific work of al-Swaidani et al. [25].

Four concrete mixes have been prepared using the same constituents and procedure followed by the author in his recently published work [25]. Concrete cubes (150 mm) were cast for the determination of compressive strength and water permeability. Concrete cylinders of (75 mm×150 mm) and (100 mm×200 mm) were also cast for testing the concrete porosity and the concrete chloride ion penetrability, respectively. The RC specimen for the accelerated corrosion test was 100 mm×200 mm concrete cylinder in which 14 mm diameter steel bar was centrally embedded. The steel bar was embedded into the concrete cylinder such that its end was at least 45 mm from the bottom of the cylinder, and it was coated with epoxy at the exit from the concrete cylinder in order to eliminate crevice corrosion.

Four zinc phosphate baths were prepared; conventional bath or mono-cation bath without modifying elements, and three bi-cation baths modified either by nickel (Ni<sup>2+</sup>), copper (Cu<sup>2+</sup>) or manganese (Mn<sup>2+</sup>) cations. Their chemical compositions and designations are illustrated in Table 1. All the chemical reagents applied in the present work were analytic grade. Deionized water was used in all zinc phosphating baths. Phosphating process was carried out by the conventional immersion of reinforcing steel specimens at 55-60 °C, for 15 min in the phosphating baths at pH value of 2±0.1. The phosphating process primarily included pre-cleaning, activation, phosphating, rinsing and drying. The chemical composition of steel rebar with some mechanical properties are presented in Table 2.

**Table 1.** Chemical composition of the prepared zinc phosphating baths.

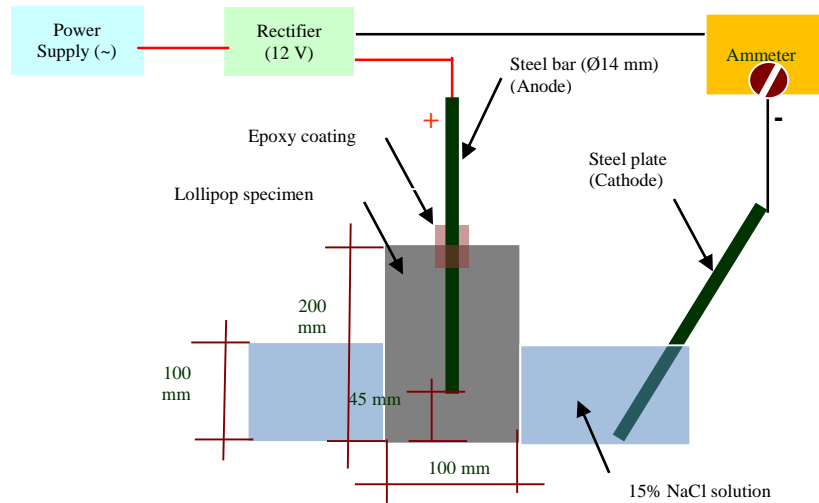
Bath type	Designation	Concentration (Mole/l)					
		$\text{PO}_4^{3-}$	$\text{NO}_3^{1-}$	$\text{Zn}^{2+}$	$\text{Ni}^{2+}$	$\text{Cu}^{2+}$	$\text{Mn}^{2+}$
Mono-cation bath (conventional)	P-Zn	0.34	0.14	0.17	0	0	0
Bi-cation baths	P-Zn-Ni	0.34	0.14	0.17	0.017		
	P-Zn-Cu	0.34	0.14	0.17		0.017	
	P-Zn-Mn	0.34	0.14	0.17			0.017

The morphology of the obtained zinc phosphate coatings were studied by scanning electron microscope (SEM, VEGA II TESCAN) and energy disperse X-ray (EDX) spectrometer. The compressive strength development of concretes was conducted on 150 mm cubic concrete specimens in accordance with ISO 4012, at ages of 28 and 90 days. Concrete permeability measured in terms of depth of water penetration was carried out as per the standard EN 12390-8. The rapid chloride penetrability (RCP) test was conducted in accordance with ASTM C1202. Three cylinder specimens of each concrete mix were tested after 28 and 90 days curing. Porosity measurements were conducted using vacuum saturation method in accordance with RILEM CPC 11.3. The results reported represent the average of six reading for compressive strength test and the average of three readings for all other tests.

**Table 2.** Chemical composition with some physical characteristics of the steel bars used in the experiments.

Rebar type	Chemical composition (%)							Mechanical properties		
	C	Si	Mn	P	S	Ni	Cu	Elastic point (MPa)	Tensile strength (MPa)	Elongation (%)
14 mm (RB 400)	0.23	0.11	0.54	0.006	0.009	0.001	0.001	488.7	638.2	15

A rapid corrosion test was used to compare the corrosion performance of NP-based cement concrete in which straight phosphate rebars are embedded, as shown in Fig. 1. Similar techniques with little differences were reported by other researchers [17, 26-30]. In the study, RC specimens were immersed in a 15 % NaCl solution leveling the half of the concrete cylinder and the steel bar (working electrode) was connected to the positive terminal of a DC power source while the negative terminal was connected to a steel plate (counter electrode) placed near the concrete specimen in the solution. The corrosion process was initiated by impressing a relatively high anodic potential of 12 V to accelerate the corrosion process. The specimens were monitored periodically to see how long it takes for corrosion cracks to appear on the specimen surface. The current readings with time were recorded at 3 h-intervals. Three specimens from each concrete mix and phosphating bath were tested after 28 and 90 days curing.

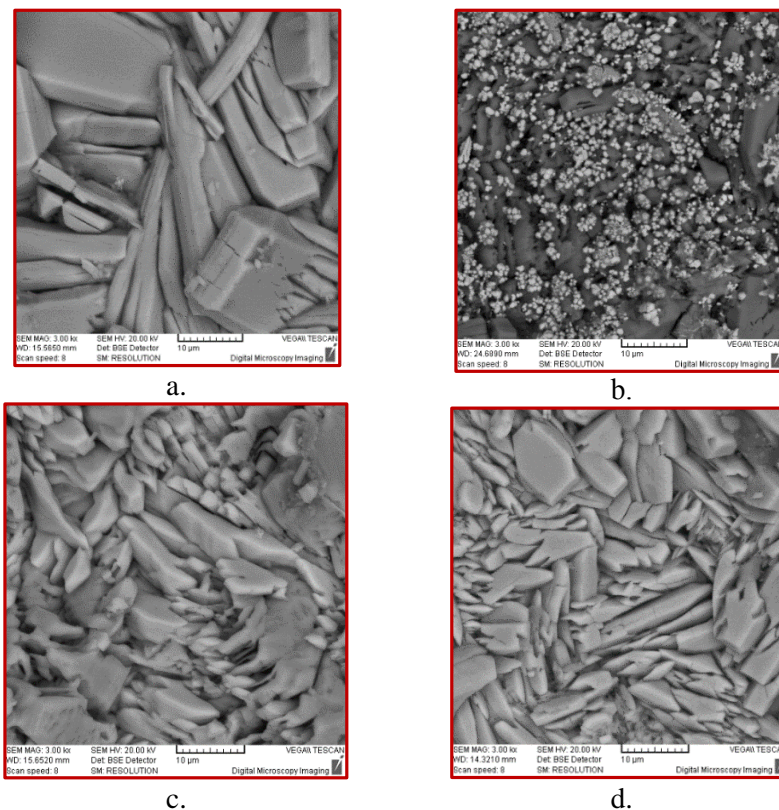


**Figure 1.** Schematic representation of experimental setup for the accelerated corrosion test.

In the study, the concrete cube specimens were tested to determine the bond strength between steel rebars and concrete using the concentric pull-out test. This concentric pull out test was similar to that outlined in ASTM C 234. The pullout test was carried out using 150 mm cubic specimens with the bar centrally embedded. Deformed steel bars with 16 mm in diameter were used instead of no. 6 (19 mm) bars specified in ASTM C 234. Each mould was designed to cast one 150 mm cubic specimen as shown in Fig. 5.a. The holed cap was designed to support the bar in a vertical position. The embedment length of reinforcing bars was 72 mm (~4.5 times the rebar diameter). The required embedment length has been obtained by breaking the bond between steel and concrete using polyvinyl chloride (PVC) sleeves to cover the unembedded length. The gap between the reinforcing steel and sleeves was sealed with a silicon sealant. A digital dial indicator has been installed on the free end to measure the rebar's displacements, Fig. 5.d. A 2000 kN capacity universal testing machine was used for the pull-out testing. The bond stress ( $\tau$ ) was calculated by dividing the applied load ( $F$ ) by the surface area ( $\pi\phi l$ ) of reinforcing steel in contact with concrete, as shown in the following formula:

$$\tau = F / \pi\phi l \quad (1)$$

Where  $l$  is the embedment length (72 mm) and  $\phi$  is the diameter of the reinforcing bar (16 mm). The bond strengths at failure were determined for each concrete mixtures and curing age.



**Figure. 2.** SEM micrographs of the zinc phosphate coating. a. P-Zn bath, b. P-Zn-Cu bath, c. P-Zn-Ni bath, d. P-Zn-Mn.

### 3. Results and Discussion

The difference in the surface morphology of the phosphate coatings can be clearly observed in SEM micrographs as shown in Fig. 2. The traditional P-Zn coating appeared to be porous, consisting of platelet shaped crystallites of 30–40  $\mu\text{m}$  in length and 5–10  $\mu\text{m}$  in width, which uniformly covered the surface of the sample, Fig. 2.a. On the other hand, the presence of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mn}^{2+}$  cations in the phosphating baths resulted in the modification of the crystallite form. The P-Zn-Cu coating consists of smaller grains, the dimensions of which varied between 4 and 10  $\mu\text{m}$ . Copper, as clearly seen in Fig. 2.b., modified and refined the crystal structure and enhanced the coverage of the surface significantly. This, which was in agreement with the results obtained by Abdalla et al. [31], can be attributed to the effect of Cu-Fe galvanic couple on dissolution of iron and acceleration of crystal deposition [31]. According to the EDX analysis, the dominant element was copper. Therefore, the metal surface exposed between the formed crystals might be a surface of copper rather than the base metal. This result is in well agreement with the result of Ogle & Buchheit [32], who concluded that  $\text{Cu}^{2+}$  may deposit as copper metal on the surface.

In addition, the P-Zn-Ni coating is smoother than P-Zn coating and its structure is characterized by platelets with sizes up to 20  $\mu\text{m}$  in length and up to 3  $\mu\text{m}$  in width, as shown in Fig. 2.c. This grain refinement was also reported in literature [1, 32, 33]. It is also noted from Fig. 5.d that the P-Zn-Mn coating is well crystallized. It completely covers the steel surface and its structure is characterized by small platelets whose width is about 4  $\mu\text{m}$  and length is 15  $\mu\text{m}$ . Manganese ( $\text{Mn}^{2+}$ ) behavior, to some extent, in the phosphating bath is similar to that of  $\text{Ni}^{2+}$ , as clearly seen in Fig. 2.d. Further,  $\text{Mn}^{2+}$  may replace  $\text{Zn}^{2+}$  in the hopeite crystal lattice. The presence of  $\text{Mn}^{2+}$  in the coating may support this assumption, as reported in the EDX analysis, Fig. 2.d. This was in agreement with the results obtained by Su & Lin [34], who proposed the formation of  $\text{Mn}_2\text{Zn}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ . Rezaee et al. (2013) also



observed this formation. Adding  $Mn^{2+}$  also reduced the phosphate coating porosity and improved surface coverage which led to an enhanced corrosion resistance [13].

The results of compressive strength development for all concrete mixes containing varying amounts of NP are given in Table 3. As expected, the compressive strength of concrete containing NP-based cement decreases with the replacement level for all curing times. For instance, the compressive strength of plain concrete and concrete containing 20% NP after 28 days curing decreased from 42.1 to 34.2 MPa. This could be explained by the following: (i) the reduction of cement content in the mix with the increase of NP content; i.e. the dilution effect [17]; (ii) the slowness of the pozzolanic reaction between the glassy phase in NP and the CH released during cement hydration. However, due to the continuation of this reaction and the formation of a secondary C-S-H, a greater degree of hydration is achieved resulting in strengths after 90 days curing which are comparable to those of plain mortars [17]. For instance, the compressive strength of NP30-based concrete was found to be 23% lower than plain mortar at 28 days curing, but this reduction was only 11% after 90 days curing.

**Table 3.** Compressive strength development of concretes.

Mix type	Compressive ( $f_c$ ) strength of concretes (MPa)-normalized	
	28 days curing	90 days curing
NP0	42.1-100%	47.9-100%
NP10	40.1-95%	46.9-98%
NP20	34.2-81%	43.7-91%
NP30	32.3-77%	47.8-89%

Permeability of concrete to water is closely related to the durability of concrete. Water penetration depth can be considered as an indication of permeable and impermeable concrete [35]. A depth of less than 50 mm classifies the concrete as impermeable and a depth of less than 30 mm as impermeable under aggressive conditions [35]. Table 4 shows the water penetration depth test results for all binder types. Concrete containing NP-based binders have lower permeability than the control concrete. Further, all concrete mixes containing NP contents  $\geq 20\%$  recorded water penetration depths less than 30 mm, after 90 days curing. This can be attributed to the pozzolanic reaction of the glassy phase in natural pozzolan [17].

Porosity of concrete containing different levels of NP after 28 and 90 days curing is presented in Table 4. Porosity of all concrete mixes decreased with curing time. As natural pozzolan is incorporated, porosity decreased significantly. Porosity of the concrete containing binders with high replacement levels of NP demonstrated much lower porosity as compared to the plain concrete. The reduction in the porosity could be attributed to the pozzolanic reaction between the glassy phase in NP and the CH liberated from hydration of  $C_3S$  and  $C_2S$  [19, 36].

From the rapid chloride penetrability test results, as illustrated in Table 4, it should be noted that NP0-based concrete permitted almost 2.1 to 3.6 times the coulombs charge, compared to the concrete containing 30% NP in spite of the fact that all concrete mixes were made with similar cementitious content and water content. The improvement in the resistance to chloride penetration may be related to the refined pore structure of this concrete and the secondary pozzolanic reaction which contributes to make the microstructure of concrete denser. This improvement was confirmed by many researchers who investigated NP, particularly at later curing ages [17, 19, 36].

Typical curves of corrosion current versus time for the reinforced concrete specimens made with NP-based binders and phosphate steel rebars are illustrated in Fig. 3. As seen in Fig. 3, current–time curve initially descended till a time value after which a steady low rate of increase in current was observed, and after a specific time period a rapid increase in current was detected until failure. Almost a similar variation of the corrosion current with time has also been observed by other researchers [17, 26, 30]. The first visual evidence of corrosion was the appearance of brown stains on the surface of the specimens. Cracking was observed shortly thereafter, and it was associated with a sudden rise in the current.

Figure 4. presents the average corrosion times required to crack the specimens made with NP-based binders and treated steel rebars. Time to cracking in NP0-based concrete specimens was in the range of 87–134 h (3.6–5.6 days), whereas that in NP30-based concrete was in the range of 197–367 h (8.2–15.3 days). In addition, it was noted from Fig. 4 that the corrosion resistance of NP-based cement concrete specimens increased significantly with age while that of the plain cement concrete had a slightly increase which has also been indicated by other researchers [17, 30].

**Table 4.** Water penetration depths, porosity, chloride penetrability and pH of the investigated concrete.

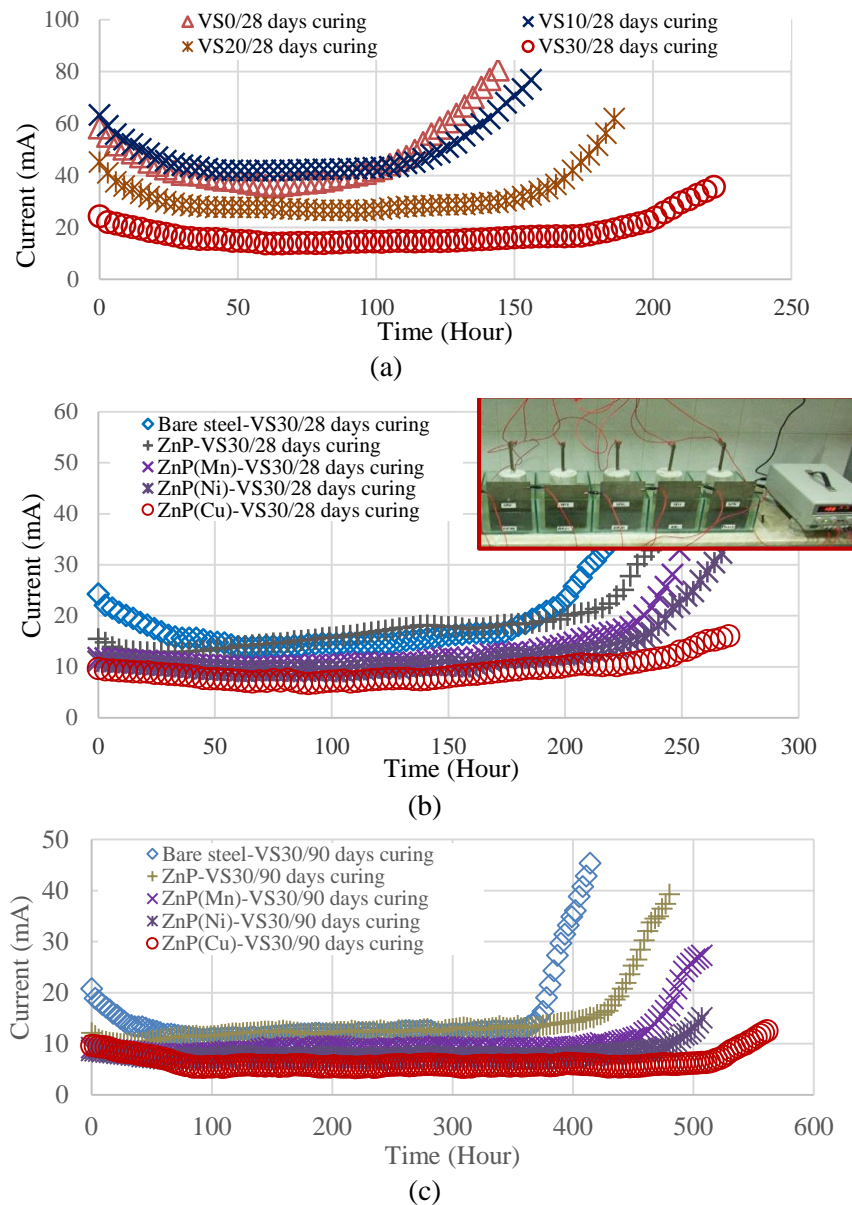
Curing time	Binder type	Water penetration depth (mm)	Porosity (%)	Chloride penetrability (Coulombs)	pH
28 days	NP0	65	17.2	6278	12.65
	NP10	61	15.7	5891	12.34
	NP20	48	14.2	4367	12.08
	NP30	42	11.1	2915	12.01
90 days	NP0	53	14.4	3971	12.57
	NP10	43	12.2	3214	12.19
	NP20	29	9.7	1965	11.91
	NP30	22	6.8	1112	11.83

The effect of using NP-based cement concrete on P-Zn coatings corrosion resistance can clearly be seen in Fig. 3(b & c). It is very clear to note that the time taken for initiation of 28 day-cured NP0-based concrete cracking was found to be 87 h for bare steel specimen. Adding NP at a replacement level of 30% increased the time taken for initiation of NP30-based concrete cracking up to 195 h. Further increase was obtained when the steel specimens were treated in zinc phosphate baths; i.e. the time taken for crack initiation reached values ranging from 213 to 261 h. In addition, the time taken for initiation of 90 day-cured NP30-based concrete cracking was found to be 367, 433, 491, 523 and 462 h for bare steel, P-Zn, P-Zn-Mn, P-Zn-Ni and P-Zn-Cu coated steel specimens, respectively. The best corrosion resistance was noted in the following system: P-Zn-Cu-NP30-based cement. The P-Zn-Cu coated steel specimens embedded in NP30-based concrete have taken about 4 times longer duration for crack initiation than the bare steel rebars embedded in NP0-based concrete. The test lasted for 261 and 523 h in this system after 28 and 90 days curing times, respectively.

This delay in corrosion time can be attributed to the following: i) the pozzolanic reaction between glassy phase in NP and CH released during cement hydration, contributes to fill the pores in concrete with an additional C-S-H. This leads to decrease of pore size and to a smaller effective diffusivity for chloride [17]. This, which was confirmed by the water penetration depth, chloride penetrability and concrete porosity tests, can also improve the long-term corrosion resistance of RC structures, and make concrete denser and less permeable [17, 30]; ii) the role of  $\text{Cu}^{2+}$  cation in refinement of the obtained coating which was confirmed by SEM & EDX analysis, Fig. 2.b; iii) the deposition of  $\text{Cu}^{2+}$ -based layer on the phosphated steel contributes to form a physical barrier between the base metal (steel) and its environment; iv) modified zinc phosphate baths enhance the alkaline stability of the obtained coatings. According to the study of Simescu & Idrissi [5], the dissolution of P-Zn-Ni coating in an alkaline medium (pH ~12.5) is accompanied by the formation of hydroxyapatite  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ . Hydroxyapatite formation occurs even in the presence of aggressive chloride ions [5]. This chemical compound provides an effective protection against reinforcement corrosion and contributes to the reduction in chloride aggressiveness [2]; v) adding NP as cement replacement reduced pH values of concrete mixes as seen in Table 4. This reduction can be due to the consumption of CH through the pozzolanic reaction and the lower cement content (i.e. the dilution effect). It is also worth to mention that the modified phosphating baths have higher corrosion resistance when compared to the traditional bath at all replacement levels of NP.

The bond stresses at failure were presented in Fig. 5. It can be clearly seen that phosphate coatings applied to the embedded steel did not significantly reduce the bond strength of steel with concrete.

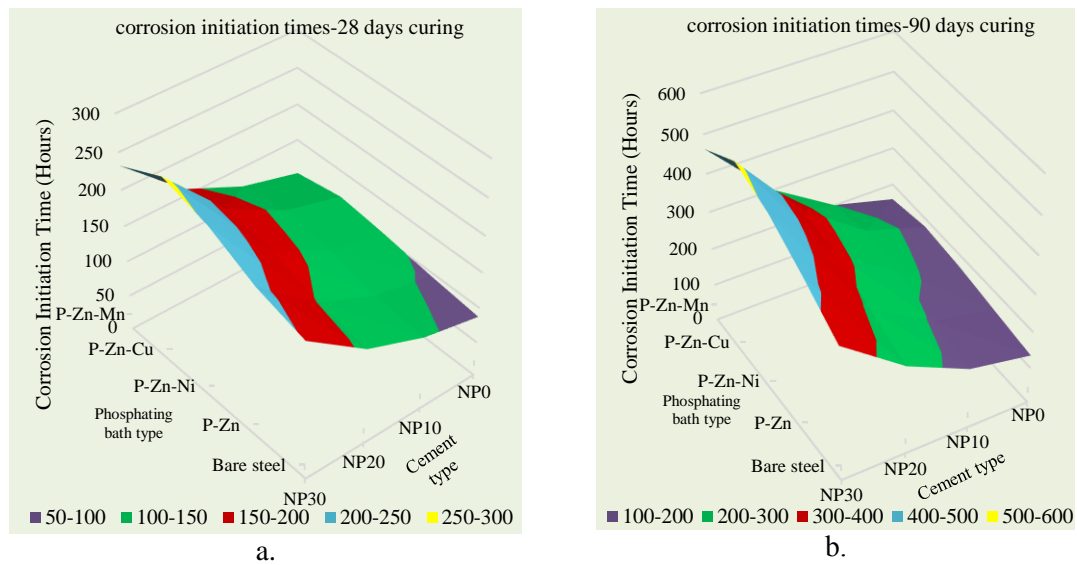
After 28 days curing, some of coatings increased the bond strength, i.e. P-Zn-Cu and P-Zn-Ni, while the others slightly decreased the bond strength with concrete namely P-Zn-Mn and P-Zn coatings. However, after 90 days curing, all treated steel specimens achieved higher bond strengths when compared to the bare steel embedded in the control concrete.



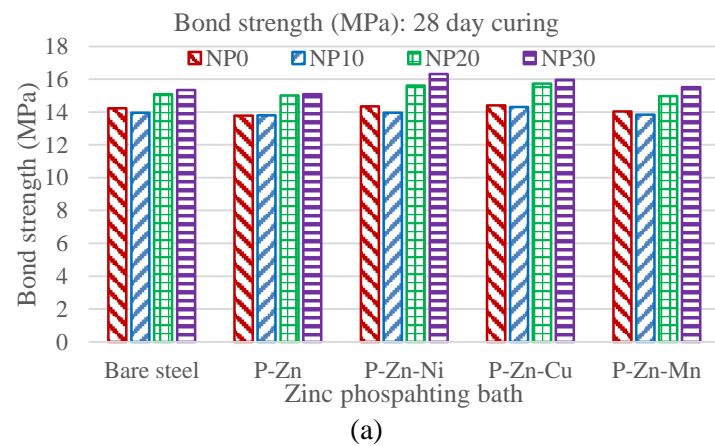
**Figure. 3.** Typical curves of corrosion current versus time of concrete a. bare steel after 28 days curing; b. NP30-P-Zn system after 28 days curing; c. NP30-P-Zn system after 90 days curing.

Fragments of NP0 and NP30-based paste specimens broken off and washed with acetone were examined and analyzed by SEM technique. Figure 6 presents the SEM micrographs of the studied pastes after 28 days curing. It is clearly seen the effect of adding NP on modifying the microstructure of NP-based pastes.

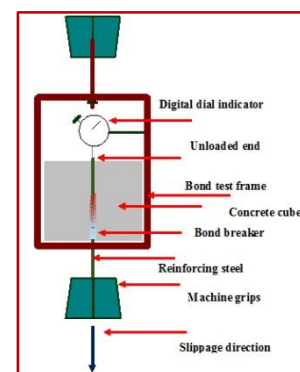
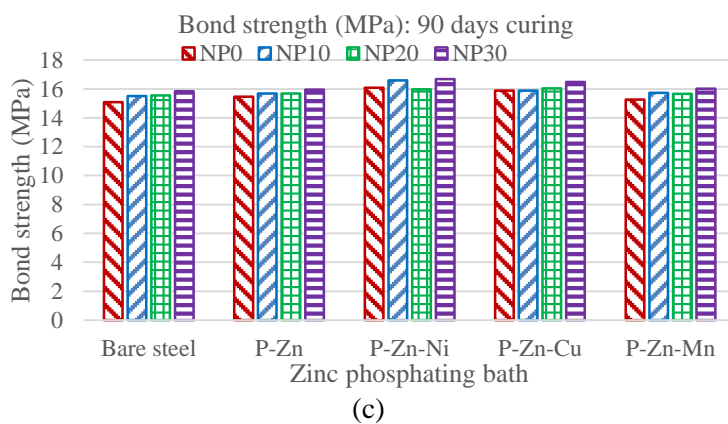




**Figure. 4.** The average corrosion times required to crack the specimens made with NP-based binders and treated steel rebars after 28 (a) & 90 (b) days curing.



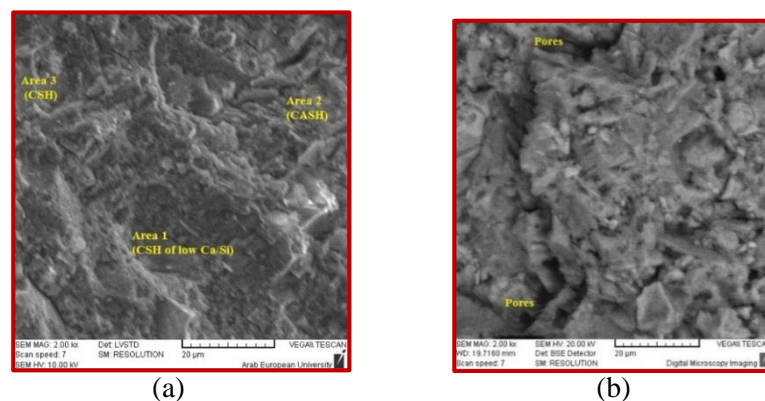
(b)



(d)

**Figure. 5.** Bond strengths of concrete for various cement types and zinc phosphate baths; (a) 28 days curing, (b) 90 days curing (a & b) and photo of the mould with a Sketch map of the bond set up (c & d).

As shown in Fig. 6.a, the SEM microanalysis of NP30-based paste showed a very dense structure and indicated that the examined fractured sections mainly consist of C-S-H and C-A-S-H phases with very low CH content which might be consumed through the pozzolanic reaction. On the other hand, as clearly seen in Fig. 6.b, darker areas were more frequent in case of NP0-based paste, indicating its higher porosity when compared with the other.



**Figure 6.** SEM analysis of 28 days-cured paste. a. NP30-based cement; b. NP0-based cement.

#### 4. Conclusions

The current paper was an attempt to investigate the effect of using NP-based cement on the reinforcement corrosion resistance of P-Zn coatings.

- Adding NP at 30% replacement level to concrete in which bare steel embedded, increased the time taken for crack initiation by about 2.25-2.75 times when compared with that of plain concrete after 28 and 90 days curing, respectively. Further increase was clearly observed when the embedded steel was treated in one of the phosphating baths, particularly in the modified zinc phosphating baths.
- Modified P-Zn baths, led to further improvements in the zinc coating performance in terms of reinforcement corrosion resistance and the bond strength between concrete and steel. The best corrosion resistance was observed in P-Zn-Cu-NP30-based cement system. It takes corrosion initiation periods 4 times longer than the bare steel-NP0-based cement system.
- Based on the results of bond strength, it should be noted that the hydrogen embrittlement which can be encountered in acidic baths, may be considered negligible in the studied phosphating baths.
- The results obtained suggest that phosphating baths modified either by copper, nickel or manganese cations may perform well even in highly aggressive environments.
- Further studies on the chemical stability of the modified zinc phosphate coatings on reinforcement are recommended. Long-term tests are also encouraged.
- Electrochemical investigations such as OCP, potentiodynamic and EIS, etc. in simulated pore solution with further analysis using XRD techniques are highly recommended.
- There is also a need to develop an optimum chemical composition of the phosphating bath, and treatment conditions that provide maximum protection against reinforcement corrosion.

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