

Modified zinc phosphate coatings: a promising approach to enhance the anti-corrosion properties of reinforcing steel

Abstract

Zinc phosphate conversion coatings are widely used for increasing corrosion resistance and surface preparation for painting. This kind of treatment has recently been introduced in the field of reinforced concrete. However, the disadvantage in the use of such coatings is the existence of pores. Zinc phosphating baths have constantly been developed and modified by additives in order to enhance the coating characteristics including the corrosion resistance and the alkaline stability. These additives and their effects on the resulting coating were reviewed in the current paper. The mechanism of phosphate coating formation, the alkali stability of the coating and the disposal of the phosphating sludge were also briefly reviewed.

Keywords: zinc phosphate coating, reinforcing steel, corrosion of reinforcement, phosphating bath additives, concrete

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Aref M al-Swaidani

 Faculty of Architectural Engineering, Arab International
 (Formerly European) University, Damascus, Syria

Correspondence: Aref A al-Swaidani, Associate Professor,
 Faculty of Architectural Engineering, Arab International
 (Formerly European) University, Damascus, Syria,
 Email a-swaidan@gmail.com; a-swaidani@aiu.edu.sy

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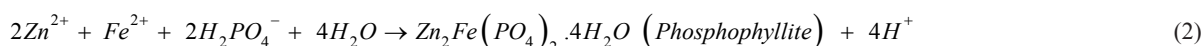
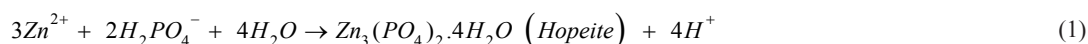
Introduction

Reinforcing steel embedded in fresh concrete develops a protective passive layer on its surface. This layer, which is formed as result of high alkalinity of the concrete pore solution (pH~13), consists of $\gamma\text{-Fe}_2\text{O}_3$ adhering tightly to the steel. As long as that oxide film is present, the steel remains intact.¹ However, chloride ions attack and concrete carbonation can destroy the film and, in the presence of H_2O and O_2 reinforcement corrosion takes place. Chloride ions, which were described by Verbeck² as the specific and unique destroyer, can be present in concrete either through the use of contaminated aggregate, sea water, brackish water or admixtures containing chlorides.¹ In the literature, there are state of the art review studies on numerous methods of protection against reinforcement corrosion.³⁻⁸ Applying zinc phosphate coating on reinforcing steel will probably be a vital approach in the future.⁹⁻¹⁴ The phosphating process has been known for over a century.¹⁵ It was extensively used in the automobile and appliance industries.^{16,17} This treatment primarily provides an inexpensive,^{17,18} non-toxic,^{19,20} reasonably hard, highly adherent and electronically non-conducting phosphate coating.¹⁵ The insulation properties make an important contribution to the prevention of reinforcement corrosion.¹⁴ Further, the phosphate conversion coatings are currently considered eco-friendly.²¹ However, 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 Ni^{2+} , Ca^{2+} , Mo^{2+} , Cu^{2+} and Mn^{2+} and nanoparticles have been extensively used to produce phosphate coatings with uniform structure, lower porosity and improved corrosion resistance and adhesion properties.^{22,13,12,23,11,17,24} Being a newly adapted method in the field of reinforcement corrosion protection^{25-27,13} this paper tries to review some important aspects related to the improvement of corrosion resistance of reinforcement using zinc phosphate coatings modified by metal cat ions or nanoparticles.

Mechanism of zinc phosphate coating formation

Phosphating is essentially an electrochemical process.²⁸ When the steel comes into contact with phosphate solution which is basically a phosphoric acid-based solution, an electrochemical reaction takes place where Fe^{2+} start to dissolve and release electrons at the anodic site, and the reduction of H^+ occurs at the cathodic site. The evolution of hydrogen and consumption of H^+ ions results in a local increase of pH at the surface leading to precipitation of zinc phosphate crystals.²⁹ According to Zimmermann,²³ Donofrio³⁰ and Kunst,³¹ the possible reactions taking place in the zinc phosphating bath are as follows:



In general, the presence of phosphophyllite is associated with a better corrosion resistance than hopeite, probably due to its enhanced chemical stability relative to alkaline electrolytes.³²

Alkaline stability of zinc phosphate coating

Studying the alkaline stability of zinc-phosphated reinforcing steel is of great importance, as it will be embedded in a highly alkaline

environment (pH~13). There are few published studies on the alkaline stability of the phosphate coating on reinforcing steel. Literature shows that the alkaline stability of zinc phosphate coatings depends on their chemical composition and crystal structure.³³ Hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) has a higher alkaline solubility than phosphophyllite ($\text{Zn}_2\text{Fe}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$).^{30,34,35} Thus, alkaline solutions first dissolve the coating composed of hopeite. Then the dissolution continues for layers rich in iron and those mainly composed of phosphophyllite.³⁶ According to the study of Simescu & Idrissi,¹³ the dissolution of zinc phosphate coating in the 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 ions¹³ Figure 1. This chemical compound provides an effective protection against reinforcement corrosion and contributes to the reduction in chloride aggressiveness.¹⁰ Elshami⁹ reported that the phosphated steel was more resistant than non-phosphated steel when exposed to alkaline solutions even in the presence of chloride ions. They attributed this behavior to the formation of a dense and protective layer composed of calcium hydroxyzincate ($\text{Ca}(\text{Zn}(\text{OH})_3)_2 \cdot 2\text{H}_2\text{O}$) which caused passivation of steel in concrete, thus contributing to a decrease in the aggressiveness of chlorides.

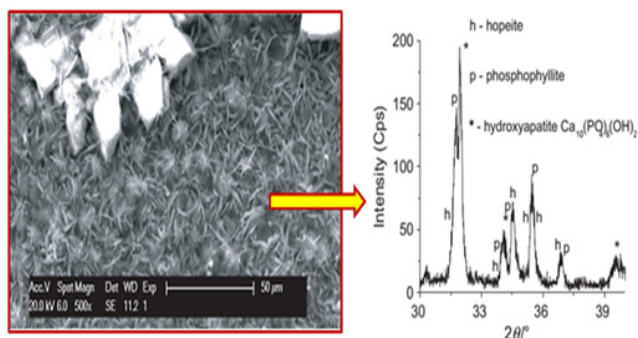


Figure 1 Scanning Electron Micrograph (SEM) of phosphated mild steel after 8 immersion days in a solution of saturated lime containing 35 g.L-1 NaCl (left) and X-ray diffraction pattern of the studied area (right).¹⁰

Effects of additives (cations, nanoparticles) on the properties of zinc phosphate coating

Different kinds of additives have been employed in the phosphating bath to improve properties of the phosphate coating. Numerous studies have explored the effects of these additives on the performance of zinc phosphate coatings. Some of these additives are metal cations such as Ni^{2+} , Ca^{2+} , Mn^{2+} , Cu^{2+} and Mo^{2+} , and nanoparticles like nano- SiO_2 ,^{11,17,21} nano- TiO_2 Shibli & Chacko,³⁷ nano- ZnO ³⁸ and nano- CeO_2 .³⁹ These additives have showed a great improvement to the final coating performance. They were also found to reduce the porosity of the phosphate conversion coating.⁴⁰

Nickel addition: The addition of Ni^{2+} ions to the phosphating bath resulted in the modification of the crystalline form, Figure 2.⁴¹ As clearly seen in Figure 2, zinc phosphate coating without Ni^{2+} addition is characterized by plates with sizes up to 30 mm in length and 10 mm in width, whereas the addition of Ni^{2+} significantly refined the crystals. This grain refinement was also reported in literature.^{42,43,9,32} In addition, Ni^{2+} played an important role in the nucleation process, probably through the ion exchange mechanism proposed by Tegehall &

Vannerberg.⁴⁴ Its presence also accelerated the surface reactions during phosphating³⁰ and improved the corrosion resistance of steel.^{45,23,46,10,14} As shown in Figure 3 & Table 1, after 8 days of immersion in a saturated lime solution containing 35 g.L⁻¹ NaCl solution, Ni^{2+} -modified zinc phosphate coating (PMS) showed a lower current density (\approx one-tenth) than mild steel (MS), and decreased the pitting susceptibility by increasing pitting potential at about 160mV compared with MS corrosion currents.¹⁰ Further, this addition improved the resistance of phosphate coating against the alkaline environment,^{13,34} i.e. Ni^{2+} ions increased the alkaline stability of phosphate layers.^{34,34} Satoh et al.,⁴⁷ studied the effects of heavy metal ion addition on zinc phosphating on electro galvanized steels and proposed the substitution of Zn^{2+} by Ni^{2+} in hopeite, such as $\text{Zn}_{(3-x)}\text{Ni}_x(\text{PO}_4)_2 \cdot y\text{H}_2\text{O}$. In a Su & Lin⁴⁰ study, the addition of Ni^{2+} in the phosphate solution promoted the impingement of Ni^{2+} , PO_4^{3-} , and Zn^{2+} . Thereby, the nucleation of the phosphate conversion coating was promoted. Thus, the Ni^{2+} can accelerate the nucleation of $\text{Zn}_{(3-x)}\text{Ni}_x(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$ grains (Figure 2).⁴⁰ According to Kulinich & Akhta,⁴⁸ Ni^{2+} has two main roles in the zinc phosphate coating mechanism. First, the rate of increase in local solution pH is limited by the slower kinetics of reactions involving Ni^{2+} compared to Zn^{2+} , leading to thinner zinc phosphate coatings when Ni^{2+} is present in the coating solution. Second, most Ni^{2+} deposition occurs during the later stages of the coating process, by nickel phosphate deposition and formation of a Ni-rich corrosion-resistant oxide (Figure 3 & Table 1).

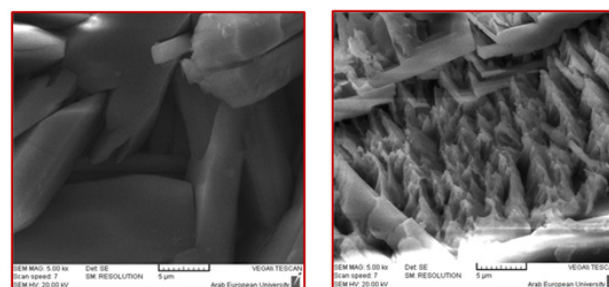


Figure 2 SEMs of the reinforcing steel samples treated in zinc phosphate bath (a) without Ni^{2+} and (b) containing Ni^{2+} .⁴¹

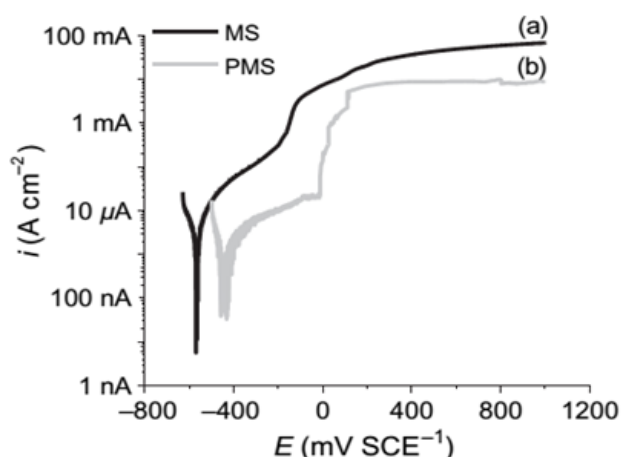


Figure 3 Polarization curves for mild steel (MS) and phosphate mild steel (PMS + Ni^{2+}) after 8 days of immersion in a solution of saturated lime containing 35 g.L⁻¹ NaCl.¹⁰

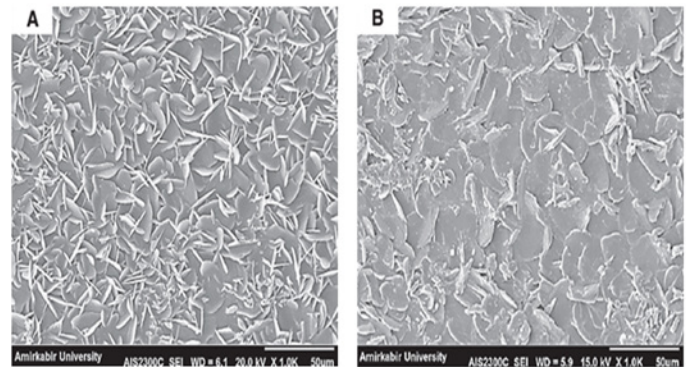
Table 1 Corrosion potentials, current densities (at corrosion potential) and pitting potentials of MS and PMS samples after 8 days of immersion in SC solution¹⁰

Sample	E_{corr} (mV ECS ⁻¹)	i ($\mu\text{A cm}^{-2}$)	E_{pit} (mV ECS ⁻¹)
Mild steel (MS)	-570	20	-180
Ni ²⁺ modified-Zinc Phosphated mild steel (PMS)	-460	2	-20

Calcium addition: Incorporation of calcium ions into zinc-phosphate bath has resulted in considerable reduction in the grain size, more compact structure and better corrosion prevention ability.^{49,50} Jalili¹² showed that adding Ca^{2+} to the phosphate bath led to a significant reduction in corrosion current to a value of about one-fifth to one-eighth when compared to that recorded by the control. This addition also enhanced the bond strength between the rebar and the concrete by about 74%. They explained this enhancement by the mechanical interlocking, which was the dominant mechanism. The zinc phosphate baths modified by calcium ions (Ca^{2+}) contain rhombic crystals of scholzite $\text{Zn}_2\text{Ca}(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$.²⁸ Zeng²¹ observed that adding calcium ions into the phosphate bath, the morphology changed from river-bed-like sheets to flower-type structure, which was more compact, crack-free and showed significant enhancement of anticorrosion properties.

Copper addition: Copper cations are basically used for their active role in the germination and growth of phosphate crystals.^{51,52} Copper also refined the crystal structure and enhanced the coverage of the surface significantly.⁵³ This was attributed to the effect of Cu-Fe galvanic couple on dissolution of iron and acceleration of crystal deposition.⁵³ Leoni⁵⁴ revealed that the addition of copper to the phosphating bath led to a drastic reduction in the corrosion rate. Kulinich & Akhtar⁴⁸ reported that adding Cu^{2+} to the zinc phosphate coating bath at concentrations up to 10ppm caused significant changes in coating morphology, adhesion, and corrosion protection. Copper sometimes replaces nickel for environment-related reasons. Although copper is considered to have nearly the same toxicity as nickel, it can be used in much lower concentration in the phosphating bath.³² According to,³² Cu^{2+} may deposit as copper metal on the surface. Therefore, the metal surface exposed between the crystals is, in fact, a surface of copper rather than the base metal.³²

Manganese addition: Manganese (Mn^{2+}) behavior, to some extent, in the phosphating bath is similar to that of Ni^{2+} . The inclusion of Mn^{2+} into the phosphate bath resulted in more ordered structure and enhanced corrosion resistance properties.^{55,47} In addition, Mn^{2+} may replace Zn^{2+} in the hopeite crystal lattice. According to Su & Lin,⁴⁰ the major role of Mn^{2+} in the phosphate treating solution is to enhance the impingement of Mn^{2+} , PO_4^{3-} , and Zn^{2+} in the solution and accelerating the formation of $\text{Mn}_2\text{Zn}(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$. Rezaee²² also observed this formation. However, contrary to the results related to the grain refinement effect accompanying with adding Mn^{2+} , Rezaee²² observed a plate-like morphology on the sample treated by the phosphate coating containing Mn^{2+} , Figure 4. This plate-like morphology of the phosphate crystals caused a higher surface coverage than needle like phosphate crystal. They showed that addition of Mn^{2+} to the phosphate bath solution caused an increase in phosphate crystal size. The competition between Mn^{2+} and Zn^{2+} cat ions to form phosphate complexes caused a decrease in the number of zinc phosphate crystals. As a result, the crystal size in the presence of Mn^{2+} became higher than that formed in the absence of the additive. In addition, adding Mn^{2+} reduced the phosphate coating porosity and improved surface coverage which led to an enhanced corrosion resistance.²²

**Figure 4** SEMs of the samples treated in phosphate bath (A) without Mn^{2+} and (B) containing Mn^{2+} .²²

Molybdenum addition: Molybdenum could be considered one of the promising compounds to be incorporated into the phosphating bath.⁵⁶ Lin⁵⁶ reported that addition of Mo^{2+} resulted in a significant corrosion inhibition capability, almost close to that of chromate conversion coatings. They attributed this enhancement in corrosion resistance to the modified morphology of coating from needle-like to fine flake-shaped structure and to the increase in coating compactness, coating mass and coverage (Figure 4).⁵⁶

Nano-silica addition: Sheng²⁴ has recently introduced SiO_2 nanoparticles in the phosphating bath as a novel accelerator. They demonstrated that with addition of these nano-particles the crystal structure of the phosphate conversion coating was refined, and the coating weight was increased resulting in a much better corrosion prevention capability. In addition, the presence of SiO_2 nanoparticles influenced the preferential orientation of the phosphate crystals and the coating morphology Sheng.²⁴ Nano-silica in the phosphating bath acts as a catalyst for the formation of more dense and compact phosphate coating on the rebar surface.¹¹ Addition of nano-silica also ensured about 11% increase in bond strength between concrete and reinforcement.¹¹ In addition, nano-silica modified zinc phosphate coated steel showed the lowest corrosion currents ($\sim 0.375 \mu\text{A.cm}^{-2}$) when compared to nano-silica free coatings ($\sim 0.535 \mu\text{A.cm}^{-2}$).¹¹ This, according to Manna¹¹ can be explained by the presence of more zinc-bearing phosphate compound in this phosphate coating as zinc-bearing phosphate compounds are less reactive to aggressive chloride solution and better insulating capability against charge transfer than the iron-bearing phosphate compounds.¹¹ The dissolution rate of iron from steel surface is slower for nano-silica containing phosphate solution because nano silica is adsorbed on the steel surface and thereby hinders the dissolution of iron.¹¹ Finally, It is worth mentioning that in the automotive industries, the phosphate conversion coating process is usually performed in a trication bath, which is mainly composed of Zn^{2+} , Ni^{2+} , and Mn^{2+} ions.^{57,14} This tri-cations zinc phosphating bath led to a significant refinement of crystals, as shown in Figure 5.¹⁴

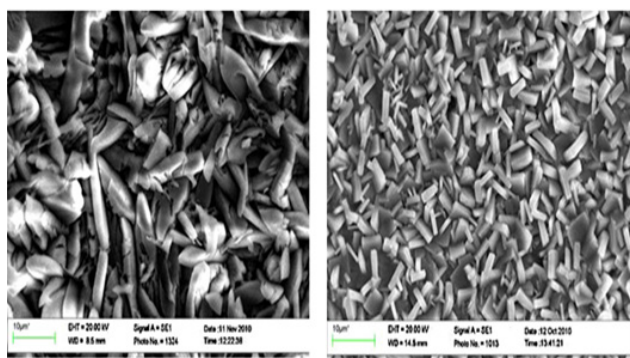


Figure 5 SEM images of the crystalline phosphate coatings on the carbon steel surface PZn (left) and PZnNiMn (right).

Sludge formation: Dissolved Fe^{3+} ions from the pickling reaction are precipitated as iron (III) phosphate as in the following reaction:³⁰



The created sludge in the process is normally filtered out from the solution utilizing some sort of filter media or equipment (Figure 5).³⁰ Phosphate sludge is a by-product that could be suitable for ceramics manufacturing. However, because of shortage of alumina and silica, it should be enriched with aluminosilicates such as clays.⁵⁸ Caponero & Tenorio⁵⁹ suggested using this sludge in cement clinker. Their results showed no damage to the clinkerization process with an addition of up to 7.0% sludge. In addition, According to Ucaroglu & Talinli,⁶⁰ the phosphate coating sludge after being treated by solidification/stabilization can be used in a matrix of Portland cement. Baldy⁶¹ also studied the possibility of reclaiming this sludge to a zinc-phosphate replenishment solution and other useful products.

Conclusion

This paper was an attempt to briefly review effects of some additives such as alkali metal ions and SiO_2 nanoparticles on zinc phosphate coating properties. Addition of certain compounds such as metal ions or nanoparticles to the zinc phosphating bath led to improvements in the zinc coating performance in terms of reinforcement corrosion resistance and the bond strength between concrete and steel. Further studies on the chemical stability of the modified zinc phosphate coatings on reinforcement are highly recommended. Long term tests when these coatings are exposed to chloride ions are also recommended.

Acknowledgments

None.

Conflicts of interest

Author declares that there is no conflict of interest.

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