Corrosion protection of reinforcement with phosphate coatings

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Abstract. As a method of protection against corrosion, the application of phosphate coatings to the surface of steel reinforcement before the manufacture of a reinforced concrete product can be considered. The influence of modifiers introduced into the cold phosphating solution on the structure and protective properties of phosphate coatings was studied. It is established that from solutions with the addition of saccharin, glucose, Trilon A, Trilon B and washing preparations, fine crystalline, dense phosphate films are obtained. The introduction of the proposed additives also reduces the time of formation of a phosphate coating on the surface of the steel and leads to a decrease in their porosity. It has been established that phosphate coatings are resistant to the effects of aqueous, salt and acidic environments. Films deposited from modified cold phosphating solutions provide better corrosion protection compared to films obtained from a traditional cold phosphating solution. Presented phosphate coatings have high protective properties, because, due to their lower porosity, they well prevent the penetration of aggressive particles to the surface of the protected reinforcement.

Keywords: protective coating, phosphate coating, corrosion of reinforcement, corrosion protection, phosphatizing.

1 Introduction

Reinforced concrete is widely known as a durable material that in most cases does not need any protection from the external environment. Steel reinforcement is usually protected by a layer of concrete. However, many facts are known when both local damage and significant destruction of the concrete coating occur, causing the corrosion process of reinforced concrete [1-6].

In concrete steel reinforcement is protected until its passive state is broken. A violation of passivity can occur for a few reasons. The main reason is concrete carbonation, as a result of which the pH of the medium becomes 9, and the corrosion process can also occur with partial carbonation at pH = 11 [7, 8]. Another reason is the pollution of the environment with harmful gases and the entry of activating ions, such as chlorine or SO₂, to the surface of the steel [9-11].

To prevent corrosion of steel reinforcement, inhibitors (nitrates and nitrites of alkaline and alkaline-earth metals) are introduced into the concrete mix, but the effect of these components decreases over time [12-16]. Also, inhibitors can negatively affect the mechanical and physical properties of concrete [17, 18]. The use of anodic corrosion inhibitors, such as NaNO₂, is also unsafe, because at low concentrations they increase the rate of steel corrosion, so their content must be strictly controlled [19-22].

Another way to slow down the corrosion process is to apply a protective coating to steel reinforcement, which would isolate it from the effects of aggressive substances [23, 24]. Such coatings can be oxide, phosphate or polymer films with good anti-corrosion properties. Phosphating is the most common industrial method of protecting steel reinforcement of reinforced concrete [25, 26].

Carbon, low- and medium- alloy steels, cast iron, aluminum and magnesium alloys, zinc and cadmium coatings, etc. can be subjected to chemical phosphating [27-29].

The essence of chemical phosphating consists in processing metals and alloys in acidified solutions of monosubstituted phosphates or monophosphates of iron, manganese, zinc, barium, calcium, etc. [26, 30].

The process of chemical phosphating is caused by hydrolysis of monosubstituted metal phosphates,
which results in an equilibrium between one-, two- and three-substituted metal phosphates and phosphoric acid. The resulting free phosphoric acid interacts with the protected metal during phosphating, resulting in the formation of sparingly soluble two-and three-substituted phosphates, which are the main component of phosphate films.

The quality of phosphate films is influenced by the acidity of the phosphating solution, its composition, metal surface preparation, technological parameters (solution temperature and processing time) [31]. The composition of phosphate films is greatly influenced by the type of cations of the phosphating solution. Films formed in a solution of manganese containing iron and zinc compounds have the best corrosion resistance [32, 33].

To accelerate the phosphating process, oxidizing agents, for example, NaNO₃, Zn(NO₃)₂, KBO₃, KClO, are introduced into the solution, as a result of which the speed of the cathodic process increases [26, 34].

An increase in the rate of the cathodic process in the presence of NO₃⁻ anions causes an increase in the rate of the film formation process and significantly reduces the formation time of the phosphate film on the metal surface. In addition, in the presence of oxidizers Fe²⁺ cations are oxidized to Fe³⁺ cations, which form iron phosphate FePO₄ with PO₄³⁻ anions [35]. It is not oxidized by atmospheric oxygen; therefore phosphate films have higher protective properties.

In practice, industrial preparation "Majef" consisting of monophosphates of manganese and iron (II) is often used for steel phosphating. The most perfect protective phosphate films are formed in 80-90 minutes in a solution containing 30-33 g/l of the drug "Majef" at a temperature of about 90 °C. Lower temperature slows down the process of film formation. In this case, large-crystalline films with low protective properties are formed. In addition, the disadvantages that limit the scope of the drug "Majef" include abundant gas evolution and, as a result, hydrogenation of the metal and the associated reduction in its ductility and strength [36].

The main reaction of hydrolytic decomposition of phosphating preparations occurs also in the absence of coated parts in the bath, which leads to an increase in the free acidity of the solution and, accordingly, to an increase in the porosity of the films and a decrease in their protective properties. Phosphating at room temperature drastically reduces the reaction rate of hydrolytic decomposition of phosphating preparations towards the formation of free phosphoric acid, which almost eliminates the dissolution of crystal phosphates formed on the surface of the metal when phosphating. However, the rate of formation of the phosphate film and its thickness in cold solutions is significantly reduced. To accelerate the interaction of the metal surface with free phosphoric acid, oxidizing agents are introduced into the phosphating solution, for example nitrates, nitrites, fluorides [26, 32-34].

Therefore, it is promising to develop solution compositions for producing protective phosphate coatings with enhanced protective properties on the surface of the reinforcement in a cold way, as well as reducing the processing time and reducing sludge formation during phosphating.

2 Materials and methods
Quantitative analysis of iron ions in an aqueous medium was carried out by the method of permanganometry. As the studied samples reinforcement made of steel grade St3 with a diameter of 10 mm was used. The protective layers were phosphate films obtained from the traditional cold phosphating solution, as well as from the developed modified solutions.

Reinforcement samples were placed for 150 days in a 3000 cm³ container filled with distilled water, 2 % MgCl₂ solution, HCl solution with pH = 5. In three tanks there were samples of reinforcement without protection, in three – samples with a phosphate film obtained from a traditional cold phosphating solution, in three – samples with a phosphate film obtained from one modified solution, in three – samples with a phosphate film obtained from another modified solution cold phosphating.

Once every three days, samples of the solution were taken from the tanks and titrated with a solution of potassium permanganate for the presence of iron ions (II).
3 Results

In a traditional solution of cold phosphating composition: "Majef" 30-40 g/l; Zn(NO₃)₂ 50-60 g/l; NaNO₂ 3-4 g/l was added 1 g/l glycerin and 1 g/l glucose. In addition to glucose and glycerin, it is proposed to introduce other organic additives: nitrilotriacetic acid / Trilon A, the disodium salt of ethylenediaminetetraacetic acid / Trilon B. Weak organic acids and their salts, which give stable complex compounds with iron ions, are buffer additives for maintaining the pH of phosphating solutions in the range of 2.6-3.2. Their introduction not only reduces sludge formation during phosphating, but also has a positive effect on the protective properties of coatings. The introduction of OP-7 and OP-10 emulsifiers into the phosphating solution contributes to the degreasing of the steel surface and the formation of a more uniform coating. However, these substances are not safe from an environmental point of view and adversely affect human health when in contact with them. As an alternative, the OS-20 preparation is proposed, which also has an emulsifying and wetting effect, but is environmentally less dangerous.

Phosphate coatings from a standard solution and from solutions with additives (Table 1) were obtained on samples from reinforcement of the St3 grade. The coating formation time was 20 minutes.

| Components  | The modified solution No.1 | The modified solution No.2 |
|-------------|----------------------------|----------------------------|
| «Majef»     | 30 – 40                    | 35 – 45                    |
| Zn(NO₃)₂    | 50 – 60                    | 50 – 65                    |
| NaNO₂       | 3 – 4                      | 3 – 4                      |
| Glucose     | 1 – 2                      | -                          |
| Glycerin    | -                          | 1 – 2                      |
| Trilon A    | 5 – 7                      | -                          |
| Trilon B    | -                          | 6 – 8                      |
| OP – 7      | 3 – 5                      | -                          |
| OP – 10     | 3 – 5                      | -                          |
| OS – 20     | -                          | 5 – 10                     |

Organic substances introduced into the phosphating solution increase the performance characteristics of the film. Apparently, they are adsorbed on the active centers of the steel surface and thus increase the number of crystallization centers. As a result, the surface of the film acquires a finer crystalline structure compared to the film obtained from a standard solution (Figure 1). After exposure to air for 1 day, the protective ability of the film increases as a result of iron oxidation in the pores of the film [37].

![Figure 1](image)

**Figure 1.** Microphotographs (× 500) of the surface of the steel with a phosphate film after treatment in a standard solution (a), in a solution with the addition of glucose (b), in a solution with the addition of glycerin (c).
In order to determine the protective ability of phosphate coatings, samples from steel reinforcement without coating and with phosphate films obtained from different phosphating solutions were placed in different media and for 150 days samples of solutions were titrated with potassium permanganate to determine the content of Fe$^{2+}$ cations. The titration results shown in Figure 2 indicate that samples with a protective film corrode more slowly than unprotected ones.

![Figure 2: Kinetic curves of steel reinforcement corrosion process in water.](image-url)
Discussion

As seen in Figures 2-4, in solutions with samples protected by phosphate films the appearance of the first signs of the presence of iron cations occurs later than in solutions with samples not covered by films; the equilibrium state in such systems is reached faster, the iron content in the solution is lower at the time of equilibrium.

Phosphate films mechanically prevent the effect of a corrosive environment on steel. If the integrity of the protective coating is violated, local corrosion foci occur.

Figure 5 shows that after being in the water for 150 days unprotected reinforcement is completely covered with rust. Sample with phosphate film from a traditional solution have corrosion-free surface
areas (Figure 5-b), and on sample with modified phosphate coating corrosion damage is negligible (Figure 5-c).

![Figure 5. Pictures of reinforcement samples after exposure to water: a) without coating; b) treated in a traditional phosphating solution; c) treated in a modified phosphate solution No. 2.](image)

Modifiers introduced into the composition of phosphating solutions improve the anticorrosive properties of coatings, reduce the likelihood of their cracking under internal stresses. It is obvious that samples coated with a phosphate film from a solution with additives lose less in mass than samples treated in a traditional phosphating solution.

Thus, for effective protection of reinforcing steels from corrosion, it is expedient and cost-effective to modify existing traditional phosphating solutions in order to improve the structure and properties of coatings, as well as reduce the energy consumption of the process, which is achieved by conducting it in a low temperature range.

5 Conclusions
During the experiment, it was found that the phosphate film protects the reinforcement mechanically, therefore, the violation of the integrity of the coating leads to the development of a local corrosion process in the area where the film is absent.

Coatings obtained from modified solutions of cold phosphating better prevent the entry of aggressive particles to the surface of the reinforcement. They have a finer crystalline structure, which does not reduce the adhesion of reinforcement to concrete.

It is obvious that additional protection of reinforcement in concrete by applying a phosphate coating will ensure the required durability of reinforced concrete structures in mass construction.

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