Use of Repeated Fluoropolymer Suspensions to Obtain Composite Electrochemical Coating Based on Zinc

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Abstract. This article deals with the issues of utilization of the waste products of fluoropolymers, namely, the suspensions of fluoroplasts that have lost their consumer properties. Such waste is recommended to be used as a filler of zinc coatings to provide increased corrosion resistance. Using the method of mathematical planning of the experiment, the authors establish the optimal compositions of galvanizing chloride-ammonium electrolytes to obtain the corrosion-resistant composite electrochemical coatings (CEC) of zinc-fluoropolymer. As a result, coatings with a finely crystalline structure were obtained differing in the distribution pattern on the surface of the samples and depending on the variation in the zinc concentration in the electrolytes. The samples of steel reinforcement with the zinc-fluoropolymer coating were tested on corrosion resistance. The increase of anticorrosive properties in CEC zinc-fluoropolymer and a slight decrease in microhardness were indicated.

1. Introduction
Utilization of production and consumption wastes as products of modern industry and used materials of the national economy is an actual scientific and technical task aimed at reducing the negative impact of polluting substances on the environment. In addition to developments in the field of effective methods of waste disposal, issues and resource-saving are urgent. One of the priority directions of waste management together with measures for their safe handling in appropriate national laws and state standards [1-3] is the recycling of waste into industrial production, which is aimed at resource saving—activities (organizational, economic, technical, scientific, practical, informational), methods, processes, a complex of organizational and technical measures and activities that accompany all stages of the life cycle of products and aimed at rational use and saving resources.

2. Literature review
The field of construction deals with waste (secondary resources) more often. Thus, in the production of silicate materials (ceramics, bricks, concrete mixtures, etc.), waste from the operation of thermoelectric power station (slag, fly ash) [4-6], metallurgical waste (metallurgical sludges) [7] and chemical and petrochemical industries (wastes of mineral industries, organic synthesis, etc.) [8,9], wood chemical industry (wood processing materials, ashes) is used. Often, the use of so-called repeated resources for the preparation of target mixtures in construction is reduced to the introduction of small portions of pre-treated waste (neutralization, grinding, purification, etc.). At the same time, great attention is paid to preventing deterioration of the performance characteristics of the target
mixtures with a reduction in the costs of their production. The most optimal method is involving waste, when no additional costs are required for their processing.

The erection of reinforced concrete structures is one of the dynamically developing directions in construction. In this case, the use of reinforcement in times increases the reliability of concrete structures and their mechanical integrity. In turn, the strength of reinforcing bars provides strength and durability of the support system of concrete structures. The strength of reinforcing bars ensures the strength and reliability of the supporting system of concrete structures. According to [10], the durability of reinforced concrete structures is also ensured by primary protection due to improving the properties of the reinforcement. Corrosion of reinforcement (rusting) occurs as a result of the chemical and electrolytic effects of the environment when exposed to liquid or solid media containing ions that are aggressive to steel (for example, Cl\(^-\), SO\(_4^{2-}\), CO\(_3^{2-}\)). The reinforcement corrosion product has several times more volume than the reinforcing steel and creates a significant radial pressure on the surrounding concrete layer. In this case, there are cracks and concrete splits with partial exposure of the reinforcement along the reinforcing bars [11]. It can lead to the destruction and possible collapse of the structure.

Currently, the problem is solved with the help of galvanized reinforcement. Galvanized reinforcement is a steel product coated with a layer of zinc to protect against the negative effects of corrosion to strengthen the supporting system of concrete structures. The main advantage of galvanized reinforcement is the presence of a zinc coating, due to which the reinforcing bars are protected from corrosion. This makes it possible to use it with high humidity, any temperature regime, and also under the influence of an aggressive environment. Due to the zinc coating, the structure does not collapse and has its original appearance for a long time [12].

Galvanizing of reinforcement can be made in the factory at the production of reinforcing bars, reinforcement grids (hot, thermal diffusion galvanizing, etc.), as well as directly on the construction site (cold galvanizing, etc.). Zinc coatings, regardless of the application method, provide electrochemical and mechanical protection of reinforcing steel.

There are several ways of applying zinc coating on the steel surface: hot and cold galvanizing, thermal diffusion and electrochemical galvanizing. The method of application is selected depending on the complexity of the molds, the required thickness of the coating, and the material from which the coated article is made.

Improving the performance characteristics of coatings based on various metals is possible due to the introduction of special fillers in their matrix [13]. So, zinc-filled coatings are more corrosion-resistant. Nanodiamonds, metal oxides, colloidal graphite, polymeric additives, etc. can be used as fillers [14,15], but in view of the fact that the most expensive materials are used as fillers, such compositions are not widely used.

The use of waste products is actual. Such wastes include liquid wastes of production of fluropolymers (FP) - mother liquors for the production of fluoroelastics and fluororubbers that remain after polymerization, washing and pressing of polymers, as well as fluoroelastic suspensions that lost their consumer properties due to prolonged storage and subsequent dispersion of the dispersion in the aqueous phase. The composition of such wastes includes the dispersed phase in the form of FP particles, a sufficiently large number of surfactants introduced into the reaction mixtures to stabilize emulsions and suspensions.

Such waste is most optimally used in the electrochemical deposition of metal coatings, which is connected with the electrophoretic mobility of the dispersion particles [16]. In view of the increased chemical resistance of the FP to most of the chemicals, the CEC based on zinc is distinguished by increased corrosion resistance due not only to the tread protection of the steel substrate from the corrosive medium but also to the barrier mechanochemical.

3. Methods of research

Determination of the optimal composition of electrolytes deposited by CEC was carried out by mathematical design of the experiment with the construction of a matrix for the planning of the full
factor experiment, calculation of the reproducibility of the experiments, the significance of the factors and the adequacy of the model [17].

The preparation of the surface of steel rods included chemical degreasing, etching and activation. The application of the CEC was carried out in an electrolytic cell of a given size. As anodes, soluble zinc plates were used. After electrolysis, the samples were rinsed and sent to a drying cabinet.

To study the surface structure of samples at the micron and submicron levels, a scanning electron microscope JEOL JSM-6510 LV was used.

Tests of coatings for corrosion resistance were carried out in a 3% solution of sodium chloride at a temperature of 18-20 °C. After keeping the images in solution, they were removed at regular intervals, the mass was determined, and the number of corrosion points was calculated [18].

The microhardness was measured on a PMT-3M microhardness instrument by pressing the Vickers diamond tip into the test material [19].

Tests of the electrolyte on the determination of the scattering capacity (SC) were carried out in a slot cell to determine the SC. The thickness distribution of the coating was measured using a demountable cathode [20].

4. Results of experimental studies
Using the method of mathematical experiment planning [17], optimal electrolyte compositions were determined for the preparation of CEC zinc-FP. The optimization parameter for the composition was the zinc current output (BTZn) and the appearance of the coating (uniformity of the surface, degree of crystallinity), and corrosion resistance. As the samples for the coating, reinforced steel bars of AIII class with a diameter of 10 mm and a length of 100 mm were used.

Table 1 shows levels and intervals of factor variation for the matrices of the planning of the full factorial experiment.

**Table 1.** The Levels and intervals of variation of the electrolyte composition for a complete factorial experiment.

| Factors          | low value (-1) | mean value (0) | high value (+1) | Dimension |
|------------------|----------------|----------------|-----------------|-----------|
| Chloride zinc    | 30             | 65,0           | 100             | g/l       |
| Boric acid       | 25             | 27,5           | 30              | g/l       |
| Suspension F-4MD | 0              | 5,0            | 10              | g/l       |

Table 2 presents the optimal compositions of the chloride-ammonium electrolytes of galvanizing with the addition of repeated suspension FP (fluoroplastic suspension F-4MD).

**Table 2.** Parameters of application and characteristics of the obtained CEC zinc-FP.

| Electrolyte composition | Application parameters | BTZn, % | Maximum fraction of dispersed phase, mass |
|-------------------------|------------------------|---------|------------------------------------------|
| ammonium chloride – 190 g/l; zinc chloride - 30 g/l; boric acid - 30 g/l; PT - 1 ml/l. | t, °C – 18-25; pH 5-5,5; | 88-98 | 11,0 |
| ammonium chloride – 190 g/l; zinc chloride - 100 g/l; boric acid - 30 g/l; PT - 1 ml/l. | cathode current density - 1,5 A/dm² | 99,6 | 4,6 |
The microstructure of the obtained CEC, established using the scanning electron microscopy method, is shown in Figure 1.

![Figure 1. Microstructure of CEC zinc-FP (ZnCl₂ – 30 g/l) (a) and CEC zinc-FP (ZnCl₂ – 100 g/l) (b) with an increase of 1000 times.]

The introduction in zinc electrolyte of a FP leads to the formation of finer crystalline precipitates, and from the electrolytes with a high content of zinc, a rounded surface structure it is noted.

The results of testing the samples for corrosion resistance are shown in Figure 2.

![Figure 2. Change in coating thickness (δ, μm) as a function of the time of action of the NaCl solution (τ, hr) n the zinc coating (1), in the CEC zinc (ZnCl₂ – 30 g/l) -PP (2) and in the CEC zinc (ZnCl₂ – 100 g/l)-FP (3).]

Thus, it is seen from the presented dependence that the introduction of the FP increases the corrosion resistance of the coating. It has been established that the CEC zinc-FP obtained from electrolytes with a maximum zinc content and a fraction of the dispersed phase of up to 5% are more resistant to aggressive media. The first corrosion marks on CEC zinc-FP (ZnCl₂ - 30 g /l) appeared after 786 hours of testing, which exceeds the standard zinc coatings, where corrosion marks appeared after 693 hours.

It was found that with an increase in the fraction of the dispersed phase in the CEC of zinc-FP, a slight decrease in the microhardness of the coating was observed. At the same time, the microhardness for Zinc-PTFE CEP obtained from electrolytes of the optimal composition does not exceed 50 kgf/mm².

It was also determined that the SC value for CEC zinc-FP relative to the standard electrolyte was slightly reduced, and was from 44 to 56%. In spite of rather low indicators of SC, it is possible to apply CEC zinc-FP on steel reinforcement in order to improve the corrosion resistance of coatings.

Figure 3 shows a reinforcement sample coated with CEC zinc-FP (ZnCl₂).

![Figure 3. The surface of steel reinforcement coated with CEC zinc-FP at an increase of 33 (a) and 100 (b) times.]

5. Conclusion
As a way to improve the performance characteristics of zinc coatings, it is proposed to introduce production waste of fluoropolymers into chloride electrowet chlorides of electrochemical zinc. The method of mathematical planning of experiments established electrolytes of the optimal composition with an FP content of 1 ml/l solution. The introduction of electrolyte in galvanizing electrolyte allows to obtain fine crystalline precipitates with corrosion resistance with a content of FP in the coating up to 5% higher than standard zinc coatings. The microhardness of CEC zinc-FP is slightly reduced relative to the standard zinc coating.

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