

PACS numbers: 68.55.Nq, 81.15.-z, 81.40.Cd, 81.65.Kn, 81.65.Rv, 82.45.Bb, 82.47.Wx

Experimental Studies of Zinc and Derivative Coatings

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Given the increasing requirements for durability and reliability of metal structures under the atmospheric and industrial corrosion, the search for effective and economically viable anticorrosion solutions becomes especially relevant. Traditional hot dip galvanizing remains a primary method for protecting steel elements. At the same time, the use of continuously zinc-coated steel products (or coatings based on zinc) is promising for low-corrosivity environments. Recently, there has been growing interest in zinc alloys with magnesium and aluminium due to the manufacturers' claims of improved anticorrosion properties with thinner coating layers. Often, this interest is also driven by the regional localization of production of such coatings. However, for the correct comparison of the service life of all types of zinc coatings and their derivatives, it is critically important to perform comparative evaluations of coating behaviour in aggressive environments for systematic analysis of quality, durability, and verification according to international standards. The aim of this work is to conduct a comparative assessment of the corrosion resistance of zinc coatings and their derivatives applied by various methods under accelerated climatic testing conditions, as well as to analyse the effect of coating thickness on the effectiveness of steel protection against

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Citation: A. V. Antonov, S. I. Ivashchenko, D. O. Bosyi, I. Y. Potapchuk, and O. I. Sablin, Experimental Studies of Zinc and Derivative Coatings, *Metallofiz. Noveishie Tekhnol.*, 48, No. 2: 169–183 (2026), DOI: [10.15407/mfint.48.02.0169](https://doi.org/10.15407/mfint.48.02.0169)

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atmospheric corrosion. As a result of the experimental studies, the prerequisites for the formation of approaches to optimising protective coatings for steels, depending on the operating conditions and their required service life, are established.

Key words: steel, zinc coating, corrosion, passivation, protection, anode, cathode.

З огляду на зростаючі вимоги до довговічності та надійності металоконструкцій в умовах дії атмосферної та промислової корозії особливо актуальним є пошук ефективних та економічно доцільних антикорозійних рішень. Традиційні гарячеоцинковані покриття залишаються основним засобом захисту крицевих елементів поряд із застосуванням крицевого прокату з цинковим покриттям (або покриттям на основі цинку), нанесені неперервною методою, є перспективними у випадках низького рівня атмосферної корозії. Останнім часом зростає інтерес до легованих цинкових стопів з додаванням Магнію й Алюмінію через заявлені виробниками поліпшені антикорозійні властивості за меншої товщини шару покриття. Часто це викликано в тому числі й локалізацією виробництв таких покриттів у певних регіонах. Разом із тим, вкрай важливим і єдиним для коректного порівняння терміну служби всіх цинкових покриттів та їхніх похідних є проведення порівняльних оцінок поведінки таких покриттів в агресивному середовищі для системної аналізи якості покриттів, їх довговічності та верифікації цих покриттів відповідно до міжнародних стандартів. Метою даної роботи є порівняльна оцінка корозійної стійкості цинкових покриттів і їхніх похідних, нанесених різними методами, в умовах пришвидшених кліматичних випробувань, а також аналіза впливу товщини шару покриття на ефективність захисту криці від атмосферної корозії. В результаті проведених експериментальних досліджень з'ясовано передумови для формування підходів щодо оптимізації захисних покриттів криць в залежності від умов експлуатації та необхідного терміну їхньої служби.

Ключові слова: криця, цинкове покриття, корозія, пасивація, захист, анода, катода.

(Received 7 July, 2025; in final version, 18 February, 2026)

1. INTRODUCTION

Zinc coatings are anodic ones; this means that the electrochemical potential of the coating metal, namely, zinc, is lower than that of the protected metal—steel. Accordingly, the zinc coating protects the base metal from corrosion through electrochemical action.

An anodic coating provides not only electrochemical but also mechanical protection. During the service life of a structure, zinc dissolves as a covering anode, thereby protecting the steel.

When zinc is applied to steel, environmental factors trigger zinc

corrosion (zinc loss), while the underlying steel becomes partially or fully protected from corrosion.

The level of protection depends on the reactivity of the coating metal: the less prone it is to corrosion, the better it protects the base metal, even those steel areas, where the zinc coating has been damaged or lost.

One crucial factor for effective protection is the reliability of the bond between the coating and the substrate (adhesion) [1, 2].

Corrosion that begins at a through-pore or scratch will remain localized if the adhesion is strong. However, with weak adhesion, corrosion products can cause the coating to peel off, leading to underfilm corrosion and blister formation.

Although zinc itself creates a protective layer over cut edges or scratches, it begins to oxidize rapidly when exposed to moisture and oxygen, forming a white deposit known as 'white rust' (Zn(OH)_2 , ZnCO_3) [1].

As corrosion products accumulate and partially fill the pores, the rate of zinc loss significantly decreases, and the resulting corrosion film provides additional protection.

Importantly, zinc retains its protective properties even at low coating thicknesses and in the presence of pores or uncoated areas. This allows for continued protection even if scratches expose the steel base.

Zinc also provides protection for edges, threads of bolts and nuts, wires, and other products, justifying the use of zinc-coated or zinc-based coated steel, including material coated by continuous methods [1, 3]. However, while the formation of corrosion products adds protection, it negatively affects visual appearance. Frequent washing or mechanical abrasion of these products can prevent the formation of stable protective compounds, reducing coating thickness. To minimize these negative effects, hot dip galvanized metal structures that are passivated after cooling to form a several nanometres thick stable barrier film.

A passive film (*e.g.*, based on Cr^+ or Si/Zr) preserves the properties of the zinc coating by limiting contact with oxygen and water, thereby reducing white rust formation, stabilizing gloss, and improving compatibility with paints or lacquers (Table 1).

2. EXPERIMENTAL DETAILS

2.1. Corrosion Resistance Studies

It is well known that, in atmospheric environments, various zinc protective coatings deteriorate at different rates [1, 3]. For this study, comparative testing was conducted using steel samples coated in accordance with Refs. [4] and [5].

To ensure the highest relevance in comparing the durability of dif-

TABLE 1. Effect of passivation on performance of zinc coatings and derivatives.

No.	Parameter	Without passivation	With passivation
1.	Resistance to white rust (salt spray chamber)	24–72 hours	> 270 hours depending on passivator
2.	Surface oxidation and dullness	Rapid oxidation, loss of gloss	Gloss retention, slower oxidation
3.	Protection in humid environments	Temporary (zinc only)	Barrier film + zinc = longer protection
4.	Appearance stability	Uneven patina, white spots	Uniform appearance, often decorative

TABLE 2. Types of samples for accelerated weathering tests.

No.	Coating type	Test sample thickness, μm	Control sample thickness, μm
1.	HDG 50	64	65.2
2.	HDG 70	92.5	94
3.	HDG 90	108.2	108.4
4.	Zn350	25	24.6
5.	Zn350PosMAC	20.6	21.2
6.	Zn450	28	28.4
7.	Zn600	35	35.6
8.	ZM120	9.9	10
9.	ZM310	18.7	18.4
10.	ZM310MA	19.9	20.4
11.	ZM430	31.1	30.6

ferent structural steel coatings under environmental exposure, the tests were conducted according to Refs. [6, 7]. The total test duration was 630 hours, with one time interval representing 70 hours.

Steel plates, measuring 150×50 mm with different protective coatings, were used as accelerated weathering test samples. The list of samples is provided below (Table 2).

2.2. Methodology of Studies

Solution Preparation. The solution was prepared by dissolving sodium chloride in distilled water with conductivity not exceeding 20 $\mu\text{S}/\text{cm}$ at $25^\circ\text{C} \pm 2^\circ\text{C}$ to achieve a concentration of 50 g/l \pm 5 g/l [7, 8].

The sodium chloride contained less than 0.001% copper and less than 0.001% nickel by mass. The sodium iodide content ranged from 0.1% to 0.5% of total impurities, based on dry salt mass.

The pH of the prepared solution was maintained between 6.0 and 7.0 at $25^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

Sample Preparation. Before testing, sample surfaces were cleaned with organic solvent using a soft brush. After cleaning, they were rinsed with fresh solvent and dried.

Sample edges and the backside were masked with adhesive tape.

Sample Placement. Samples were placed in the test chamber so as not to be directly exposed to the spray nozzle stream. They were arranged with the unprotected side facing upward at an angle between 15° and 25° . Samples did not contact the chamber and were exposed to unrestricted spray circulation. The sample support was made from inert non-metallic material.

Test Conditions. Chamber temperature was maintained at $35^{\circ}\text{C} \pm 2^{\circ}\text{C}$ throughout the test. Average solution condensate collection rate is of $1.5 \text{ ml/hour} \pm 0.5 \text{ ml/hour}$. Condensate sodium chloride concentration is of $50 \text{ g/l} \pm 5 \text{ g/l}$; pH—6.5 to 7.1.

Post-Test Sample Processing. After testing, samples were removed and dried for 0.5 to 1 hour to minimize removal of corrosion products. Before inspection, any remaining solution was carefully rinsed off the surface.

2.3. Evaluation of Test Results

The appearance of rust on the sample covering an area of more than 10% terminated the test for the specific sample, and the test completion time was recorded separately for it. All indicators were evaluated after the end of each test cycle.

The condition of metal structure coatings was assessed using two ratings in accordance with [9] based on the ability of the coating to protect the base metal from corrosion and thus prevent degradation of the base metal; based on the ability of the coating to maintain integrity and thus maintain a satisfactory appearance.

Although the functions of these two ratings overlap, they can be used separately to assess the degree of corrosion protection of the base metal (protection rating R_p) and to assess the appearance (appearance rating R_A).

The protection rating R_p was calculated using formula (1):

$$R_p = 3 \cdot (2 - \log A), \quad (1)$$

where A [%]—corrosion coverage (in %) of the sample under consideration.

The appearance rating was assigned using three components:

1) area affected by a specific defect on a scale from 10 to 0 (where 10 is the least affected);

TABLE 3. Classification of coating damage types R_A .

A	Staining or discoloration reducing coating quality (excluding visible corrosion products of the base metal)
B	Dulling with little or no visible corrosion
C	Corrosion products of anodic coatings
D	Corrosion products of cathodic coatings
E	Pitting on the surface (possibly not reaching the base metal)
F	Delamination, flaking, chipping
G	Blistering (subsurface corrosion)
H	Cracking
I	Crevice corrosion
J	Cavity formation

2) subjective assessment of the degree of deterioration of the coating (vs = very insignificant amount, s = small amount, m = moderate amount, x = excessive amount);

3) classification of types of coating damage R_A (Table 3).

3. EXPERIMENTAL RESULTS

The results of the conducted studies, in accordance with Ref. [9], are summarized below (Table 4).

At equivalent coating thicknesses, ZM-type coatings proved to be clearly more resistant to aggressive atmospheric environments compared to standard zinc coatings [10]. ZM coatings also exhibited better aesthetic appearance in the atmosphere during the initial period of operation.

As for the samples with hot dip galvanized (HDG) coatings, their high resistance to aggressive environments can be confirmed [10]. However, a characteristic of these samples is the early formation of hydroxide compounds ($Zn(OH)_2$, $ZnCO_3$), commonly referred to as 'white rust', which negatively affected the visual appearance of the sample.

After removing the loose 'white rust' deposits from the HDG samples to measure the residual coating thickness, noticeable dulling and localized wear of the zinc coating were recorded.

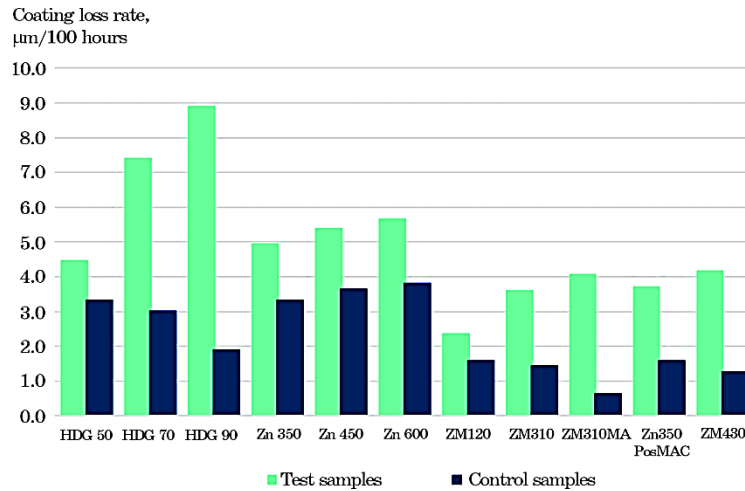
Additionally, for all sample types, which were cleaned during the test cycles, there was a trend of increased coating loss rate with increased initial coating thickness.

At the same time, control samples of all materials, which remained in the salt spray chamber and were not cleaned after each test cycle, showed partially opposite results: in some cases, the rate of coating loss was higher for thinner coatings [2]. A comparison of the coating

TABLE 4. Results of corrosion studies.

Indicators Type of coating	Thickness of zinc coating before testing, μm	Thickness of zinc coating after 630 hours testing, μm	Rate of zinc coat- ing loss on test samples $\mu\text{m}/100$ hours	% of zinc coating thickness remaining after 630 hours test- ing, μm	Time of testing, hours	Defect area, A%*	RP/RA rating
HDG50	64	28.1	4.5	56%	630	0%	10/10 vs C
HDG70	92.5	46.6	7.4	50%	630	5%	9/9.5
HDG90	108.2	56.1	8.9	48%	630	0%	10/10 vs C
Zn350	25	24.2	4.9	3%	490	25%	7/7.5 x F,C
Zn450	28	26.4	5.4	6%	490	30%	7/7 m F,C
Zn600	35	31.7	5.7	9%	560	30%	7/7 m F,C
ZM120	9.9	9.9	2.4	0%	420	60%	6/4 x F
ZM310	18.7	17.6	3.6	6%	490	10%	8/9 m F
ZM310MA	19.9	19.9	4.1	0%	490	40%	6/6 x F
Zn350 PosMAC	20.6	18.2	3.7	12%	490	15%	7/8.5 s F,C
ZM430	31.1	26.2	4.2	16%	630	10%	8/9 m F

* These rating indicators were compared at the end of the full cycle lasting 630 hours or when rust appeared on more than 10% of the sample.

**Fig. 1.** Coating loss rate for test and control samples.

loss rates for control and test samples is shown in Fig. 1.

Based on the results, it can be stated that the coating loss rate for control samples (which were not cleaned from hydroxide compounds

formed on their surfaces) was significantly lower than that for test samples.

In the case of HDG-coated samples, a correlation was observed between coating loss rate and coating thickness:

- for cleaned samples, an increase in thickness led to higher loss rates;
- for uncleaned samples, the opposite was true: the thicker the coating, the lower the loss rate, up to 4.5 times lower for HDG 90.

A similar trend was observed for the ZM-group coatings, though the effect was less pronounced.

For samples from hot dip galvanized coil, the data was more ambiguous: Zn350, Zn450, and Zn600 followed the same trend for both test and control groups. However, Zn350 PosMAC behaved more similarly to the ZM group. This may be attributed to differences in the quality of passivation by different manufacturers.

In general, based on structural heterogeneity and the electrochemical activity variations due to coating thickness, thicker coatings (regardless of the application method) tend to wear faster than thinner ones under identical conditions.

From the comparison of test and control samples (Fig. 1), it can be concluded that actual resistance of test samples in real-life conditions could be up to 2 times higher than the lab test results suggest.

Figures 2–4 show photographic images of the sample surfaces after 630 hours in the salt spray chamber. Some samples had already failed earlier, but were kept in the chamber to allow visual comparison.

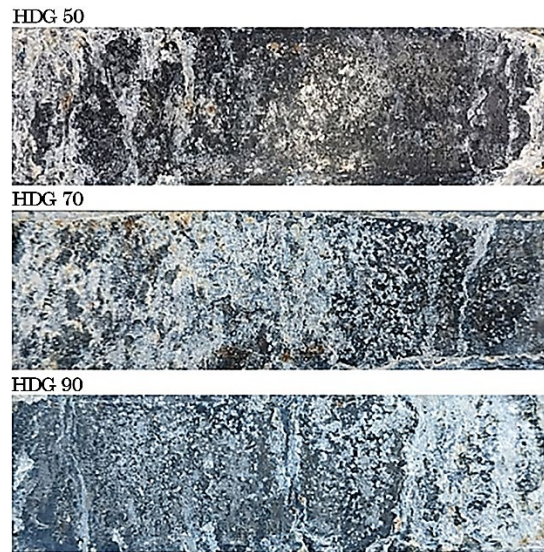


Fig. 2. Surface of HDG-type coated samples after 630 hours in the salt spray chamber.

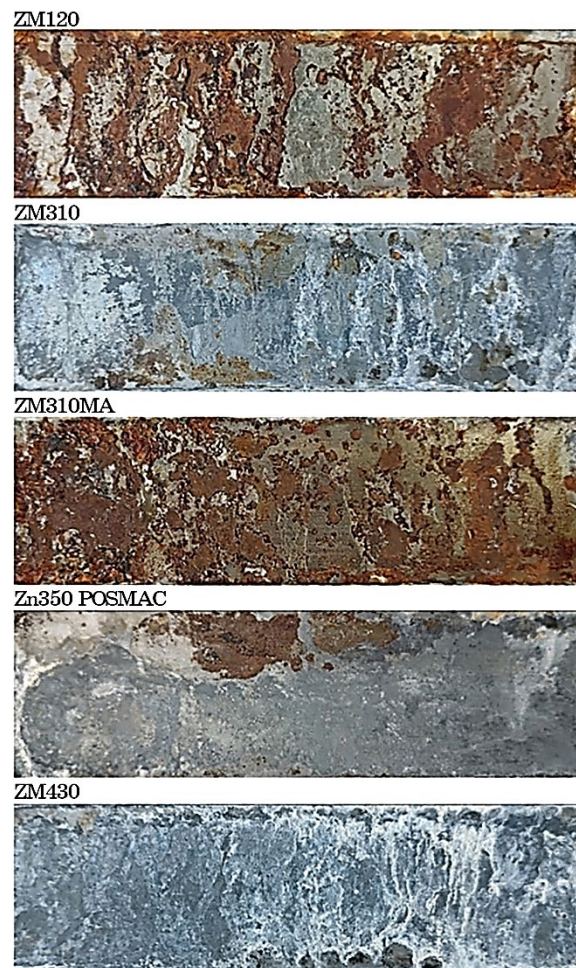


Fig. 3. Surface of ZM-type coated samples after 630 hours in the salt spray chamber.

In general, the HDG-coated samples (Fig. 2) show widespread signs of white rust, uneven coloration of the zinc surface, but the coating remained intact, indicating high resistance of this type of coating to aggressive environmental exposure. As seen in Fig. 3, some samples exhibit significant corrosion damage, including a continuous layer of red rust. However, ZM310, Zn350 PosMAC, and ZM430 were among the most resistant samples in terms of appearance. Despite having thicker coatings, Zn-type samples (Fig. 4) showed lower resistance under salt spray conditions. The likely reason is poor passivation or low quality of the base coating.

Figures 5–7 present graphical representations of accelerated weath-

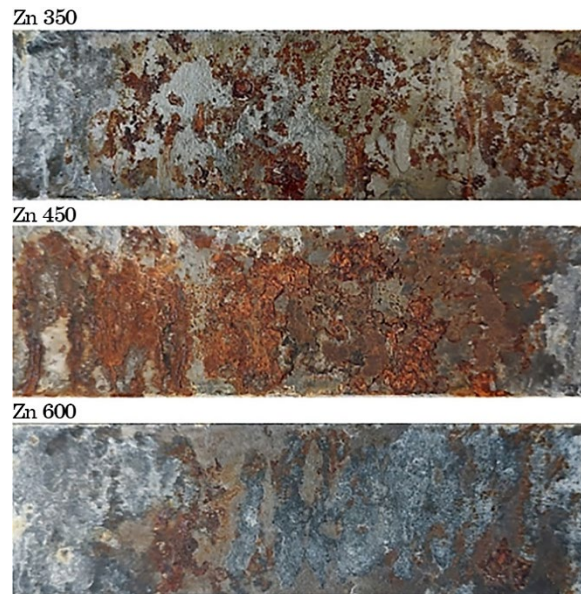


Fig. 4. Surface of Zn-type coated samples after 630 hours in the salt spray chamber.

ering tests, showing coating thickness loss over time for samples that were cleaned after each test stage.

In general, these results confirm similar trends in zinc coating wear, regardless of coating thickness or application method.

Laboratory test results based on Ref. [8] cannot serve as a direct indicator of zinc coating lifespan, but according to Refs. [4, 5], it is possible to estimate wear rates and approximate service life for various coatings.

The lifecycle of zinc coatings, according to reliability theory, can be described by a failure intensity curve and divided into three stages (Fig. 8): adaptation period ($0 \dots t_1$) with formation of corrosion products (white rust), often washed off by rain [1, 8]; normal operation ($t_1 \dots t_2$) with formation of a dense protective layer from corrosion products [8]; ageing period ($t > t_2$), when protective layer thins, coating begins to flake or peel.

The segment $0 \dots t_1$ is primarily characterized by a reduction in the thickness of the zinc coating due to the appearance of ‘white rust’ and its cyclical washing away by rain.

In the segment $t_2 \dots t_1$, coating defects may occur and are determined by random factors that affect a local area, for example, mechanical damage during installation, continuous-cyclic moisture exposure (*e.g.*, water droplets falling from PV modules onto the structure), or poor grounding of PV modules (leakage current from PV modules to the

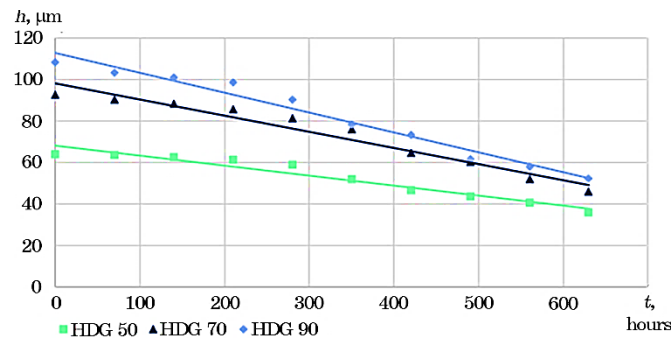


Fig. 5. Time-dependent coating wear for HDG-type samples in the salt spray chamber.

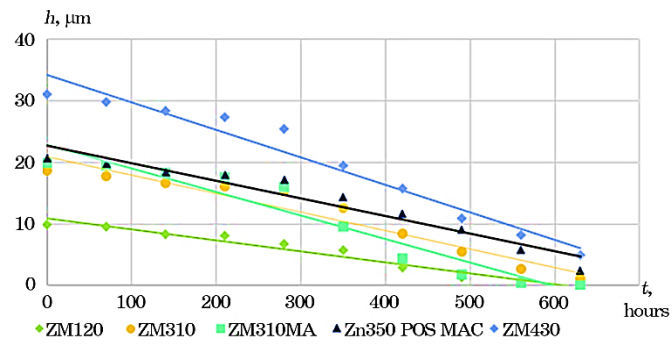


Fig. 6. Time-dependent coating wear for ZM-type samples in the salt spray chamber.

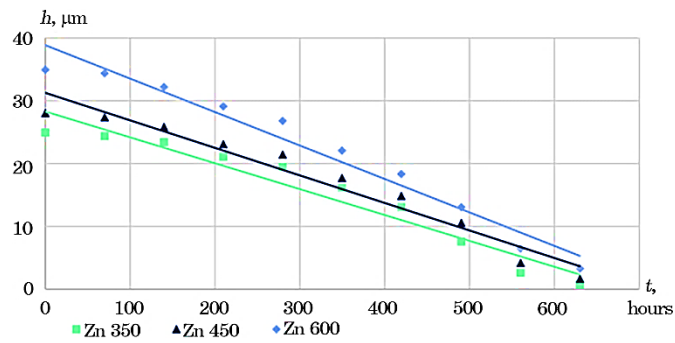


Fig. 7. Time-dependent coating wear for Zn-type samples in the salt spray chamber.

structure), resulting in zinc coating damage in the area, where leakage currents flow.

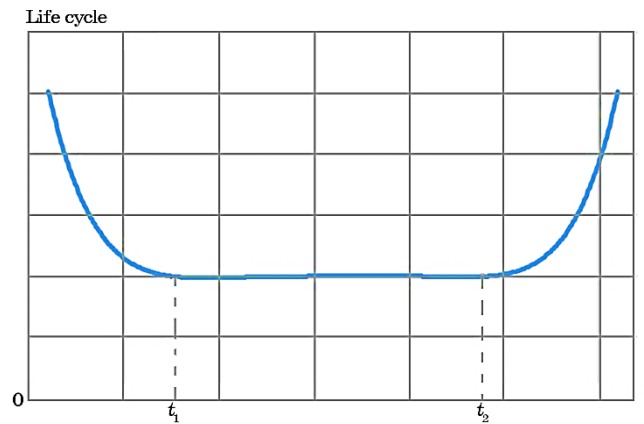


Fig. 8. Life cycle of zinc coating.

From the period $t > t_2$ onward, the frequency of coating defects increases due to long-term exposure to external factors. The mechanism of coating degradation at this stage is explained by wear and ageing models [3].

Steel structures are exposed to a combination of external factors, and corrosion-induced degradation of the coating is one of them.

In general, all types of corrosion damage follow the same principle, namely, the mechanism of corrosion is electrochemical in nature and identical for all types. The specific type of corrosion depends on factors, which accelerate the process and typically occur under abnormal operating conditions, for example, the presence of leakage currents, continuous-cyclic moisture exposure, mechanical damage, chemical irritants, *etc.* It is sufficient to generalize all of these under the umbrella of electrochemical corrosion without classifying them into subtypes.

Due to the heterogeneity in the structure and composition of metals, and the uneven distribution of the electrolyte (which is the moisture film containing dissolved chemicals on the metal surface), different areas of galvanized steel surfaces can have varying electrochemical potentials even in the absence of external electric fields. As a result, an electrical corrosion current flows within a closed loop of the galvanic couple, as shown in Fig. 9. In this situation, the more electrochemically active element (with a lower electrode potential) becomes the anode, and the less active one becomes the cathode. In this case, the zinc coating acts as the anode, and the steel substrate is the cathode. Corrosion occurs on the anode side of the galvanic couple, while the steel remains protected from corrosion (Fig. 9, *b*).

The presence of external currents can significantly accelerate corrosion. However, regardless of these factors, corrosion will still occur on

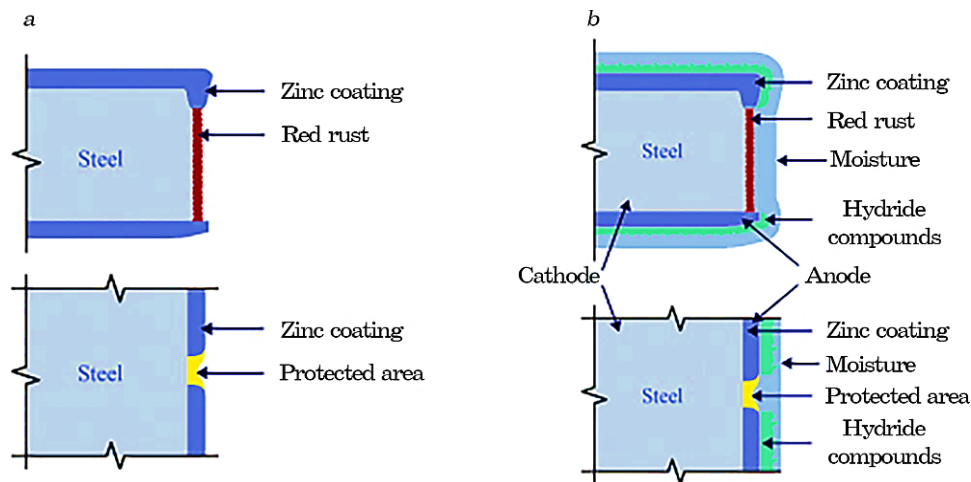


Fig. 9. Protection of the substrate (steel) with zinc coating: *a*) after production; *b*) during service.

the anode side, that is why zinc coatings and their derivatives are suitable for steel protection.

Thus, the phenomenon, in which galvanized steel samples with unprotected edges or damaged coatings do not exhibit corrosion, can be explained by the action of the zinc coating on the main part of the sample. The zinc coating provides not only electrochemical protection for the substrate, but also mechanical protection (see Fig. 9).

For structures located in corrosive soils and/or exposed to stray currents, additional corrosion protection measures may be used: passive protective anodes (Fig. 10, *a*) or active cathodic-protection systems (Fig. 10, *b*).

Cathodic protection involves creating a galvanic corrosion cell, where the anode corrodes instead of the protected structure, which becomes the cathode [7, 11–13] (Fig. 10, *a*). The anode and cathode are electrically connected.

The protective anode may be made of magnesium, zinc, aluminium, or other metals, which are more active (less noble) than the base metal. Due to the galvanic reaction, the steel does not corrode; instead, the anode dissolves. Another option is to use impressed current cathodic protection from an external DC power source (Fig. 10, *b*).

An additional factor contributing to the degradation of zinc coatings is leakage currents originating from photovoltaic modules. Under normal operation, the permissible leakage current is up to 1 mA. The dissolution of the zinc coating intensifies at the points, where the structure is in local contact with the ground. Even at such low current levels, the impact on the rate of zinc loss can be significant.

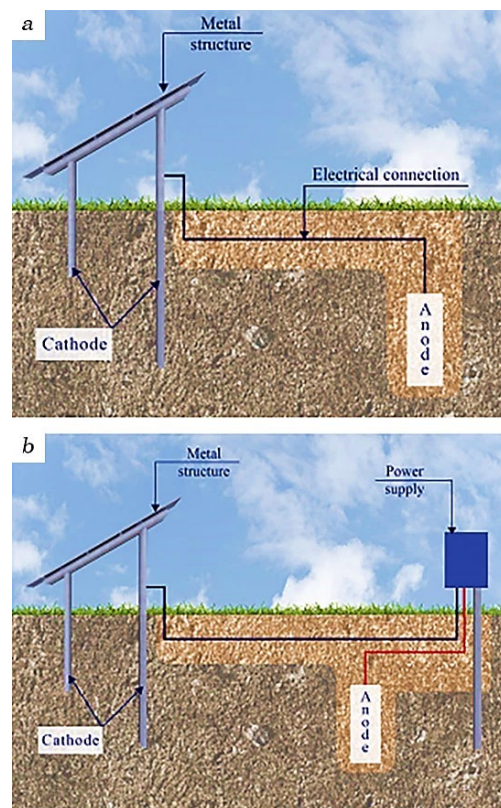


Fig. 10. Cathodic protection of metal structures: *a)* passive anode protection; *b)* active cathodic protection.

4. CONCLUSIONS

1. The conducted tests confirmed that all zinc coatings and their derivatives generally exhibit similar behaviour under comparative conditions.
2. HDG-type coatings demonstrated the highest resistance to aggressive environments, despite the fact that they also exhibited the highest rate of coating thickness loss.
3. Among the ZR- and Zn-coating groups, the ZM coatings showed greater resistance, primarily due to the high quality of passivation.
4. The application of HDG-type coatings is strongly recommended for environments with corrosivity categories C3 and C4.
5. The application of ZM and Zn coatings is recommended for environments with corrosivity categories C1 and C2.
6. To increase the service life of zinc coatings and structures, it is advisable to implement high-quality equipotential bonding of structures.

7. It is necessary to optimize the selection of protective coating types for steel, based on operating conditions and required service life.
8. The impact of leakage currents on the rate of zinc coating loss requires further research at solar energy facilities.

AUTHOR'S CONTRIBUTION

A. V. Antonov carried out development of research methodology, scientific novelty, analysis and calculations, construction of dependences. S. I. Ivashchenko conducted research and measurements. D. O. Bosyi, I. Y. Potapchuk and O. I. Sablin provided scientific consulting.

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