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Corrosion resistance of steel structures in marine conditions

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Abstract. The article is devoted to the study of the corrosion resistance of steel pile supports made of pipe steel 09Mn2Si (09G2S), under conditions of cyclic wetting (conditional waterline), where conditions are created for the occurrence of corrosion processes at maximum speeds, and also a study of the protective ability of zinc coating applied to the railing (balustrade) of a steel bridge made of carbon steel of normal quality (St3). It was the bridge structures that became the subject of research. We considered the effects of cyclic wetting, wear, and climatic factors on the materials of piled supports, fences, and coatings intended for operation in the marine structure. We investigated the corrosion resistance of the 09Mn2Si steel used as pile supports of offshore structures. We have found that the corrosion rate of the 09Mn2Si steel does not exceed 0.32 mm/year in the zone of cyclic wetting. We have confirmed that the corrosion rate of steel practically does not change in the sections with damaged coatings and does not depend on the area of the uncoated zone. Measuring the electrochemical potential of 09Mn2Si steel, we have found that short-term friction against a solid only weakly affects the corrosion rate of steel in seawater. We have proposed a methodological approach to assessing the service life of hot-dip galvanized coatings on components of steel structures made of carbon steel of normal quality (St3) intended for operation in marine conditions. A forecast of the durability of 120 μm -thick zinc coatings, expected to provide anti-corrosion protection of steel products for 60 years, was made based on the proposed technique.

1. Introduction

Aside from ships and other watercraft operating at sea, numerous onshore port facilities, fences and fixed bridges across sea straits are installed on supports. Ensuring reliability and durability of such steel structures is a major challenge; for this purpose, data on the corrosion resistance of materials under operating conditions should be obtained at the design stage [1]–[4]. Reference data are generally used to select a corrosion margin; however, the real data may differ considerably because mechanical factors such as wear can have a critical impact in addition to corrosion. To combat this, protective coatings are applied on many structures [5], [6]. The degradation of these coatings depends on their properties and a combination of other characteristics.

Reliable real data on the degree of material degradation can be obtained by conducting experimental field tests, or laboratory studies simulating the service conditions of the structure, in particular accounting for the most aggressive/critical environmental effects.

A steel pile can be schematically represented as consisting of three sections: the upper section is constantly exposed to the marine environment; the medium section is occasionally splashed with seawater; the lower section is immersed in water [7]. This difference in exposure to the corrosive environment largely

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determines the distribution and rate of corrosion in objects that are not fully immersed in water. The experience accumulated for operating such steel structures not completely immersed in seawater indicates that the maximum corrosion rates are observed in the region that is periodically exposed to water (splash zone) [8]–[10].

Fig. 1 shows the variation in the corrosion rate for a pile in the zone of cyclic wetting. Furthermore, it was established in [11], [12] that the height of the region with the maximum corrosion damage above the splash zone depends on the wave height at the site where the pile is installed. Therefore, the corrosive wear of piles in operating conditions can be assessed by determining the corrosion rate of the steel from which the piling is made upon cyclic immersion in seawater.

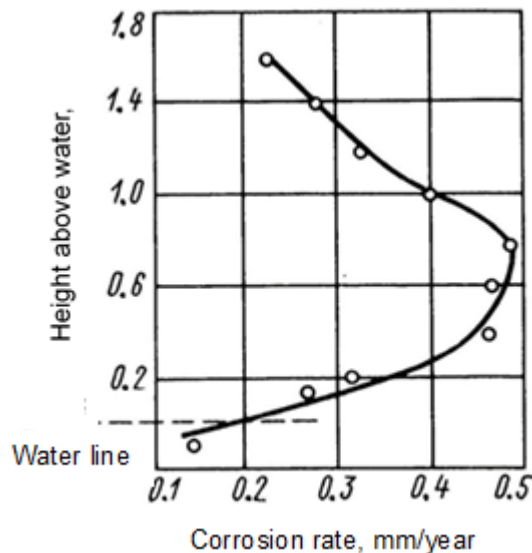


Figure 1. Corrosion rate distribution over a steel pile in the zone of cyclic wetting.

Different polymer coatings can be used to increase the service life of piled supports. If the technology for applying such coatings is exploited correctly, their protective properties are preserved for up to 10 years or more. However, an ice cover forms on most of Russia's inland seas during the winter, so protective polymer coatings of piled supports can be damaged in ice breakup, with bare metal abraded by ice. It is hypothesized that the corrosion rate of bare metal increases significantly in this case [13], which is yet to be fully confirmed experimentally. Experiments on steel wear during friction against ice were carried out in [14]–[19], finding that ice is heavily destroyed even at a 5 MPa pressure against the steel specimen that is not worn out in the process. Assuming that solid objects can be frozen into the ice, leading to mechanical wear of the surface in contact with steel, the corrosion rate of steel in this point can be increased due to the electrode potential difference generated between the mechanically worn segment and the rest of the surface, where an iron oxide film forms in seawater. Ref. [20] determined the magnitude of this potential difference and the time in which the metal surface remains 'activated' (without oxides) after the interaction with the rubbing object has stopped.

Zinc coatings are used for steel onshore structures that need to be in long-term service in the marine environment. Accordingly, the corrosion rates and the durability of the coatings for a specific climatic region should be established rather quickly. The service life of zinc coatings is proportional to their thickness regardless of the application method [10], [21], [22]. Thus, it can be assumed that corrosion of zinc coatings develops over time at an approximately constant rate, which is confirmed experimentally during 8-year tests of zinc in a tropical marine environment, including a sea coast (Fig. 5) [23].

One of the most common methods for assessing the corrosion resistance of coatings in a marine environment is the salt spray test (SST). The temperature in the salt spray chamber is constantly maintained at a level of +35 °C, and the humidity at over 90% by spraying finely atomized droplets of the salt solution, which greatly accelerates the corrosion process. Unfortunately, the results obtained by SST do not answer the question of durability of zinc coatings with a given thickness in real conditions. Full-scale climatic tests make it possible to obtain the most accurate corrosion rates, since they simulate the real operating conditions of the product and allow calculating the durability. However, their main drawback is the considerable time they take. The minimum exposure times of zinc coatings during field tests range from 3 to 8 years. Clearly, a specialized procedure estimating corrosive wear should be worked out for more rapid assessment of durability.

The goal of the study consists in estimating the durability and reliability of structures made of steel materials and steels with coatings in the conditions of the Kerch Strait, exposed to climatic, corrosive and

mechanical impacts. The objectives of the study were an experimental study of the corrosion resistance of steel bridge supports under conditions of variable wetting by sea water, including with local destruction of the paint coating and with short-term mechanical impact on an unprotected metal surface; carrying out accelerated and full-scale climatic tests of zinc-coated steel samples to determine the acceleration coefficient required to calculate the service life of coatings in long-term operation conditions.

2. Methods

The data given in literature indicate that the main critical impacts in the marine environment are cyclic wetting, corrosive abrasion wear, exposure to a salt fog. The correct testing procedure for assessing the durability of steel structures and coated metals can be selected by analyzing the climatic conditions taking into account the level of precipitation (wetting frequency) and temperature, the composition of the environment at the zone of operation, external factors (ice impact, mechanical loads, etc.) to be recreated during the tests.

2.1. Selection of the environment

Before corrosion tests with cyclic wetting can be carried out, the wetting frequency of the specimens should be selected. Fig. 2 shows the effect of the frequency of cyclic wetting in a 0.5 N sodium chloride solution for CT3 steel specimens [24].

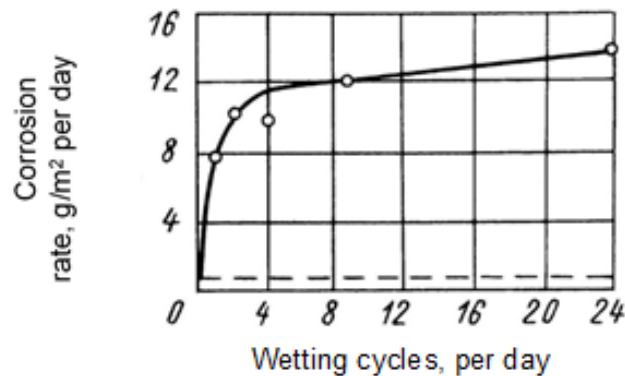


Figure 2. Effect of wetting frequency on corrosion rate for mild steel (ST3 steel).

As follows from Fig. 2, increasing the number of times that the specimens tested are wetted from 4 to 24 a day only slightly affects the corrosion rate. For this reason, the tests were carried out with the specimens periodically immersed in the solution 4 times a day.

The corrosiveness of the environment largely depends on the relatively high concentration of chloride salts, high content of dissolved oxygen and high electrical conductivity. The location of the bridge under construction in the Kerch Strait, connecting the Azov and Black Seas, was the decisive factor in determining the composition and concentration of salts for preparing the test solution. The Azov Sea is small, with a substantial freshwater runoff, making its waters slightly saline (11–13 g/l). The maximum levels of water salinity were observed in the Kerch Strait (13–15 g/l), see Table 1.

Table 1. Ionic composition of water in the Kerch Strait.

Calculated sample composition at depth of 0.7 m		Calculated sample composition at depth of 4.5 m	
Formula	Concentration, mg/dm ³	Formula	Concentration, mg/dm ³
NaCl	3396	NaCl	4457
NaHCO ₃	379	NaHCO ₃	293
CaCl ₂	75	Na ₂ SO ₄	738
CaSO ₄	598	CaSO ₄	2046
MgSO ₄	495	MgSO ₄	1015
Total	4943	Total	8546

The composition corresponding to the most corrosive environment was chosen for the corrosion tests, i.e., the total salinity was 8.55 g/l, Table 2.

Table 2. Calculated salt composition of water samples.

Reagent	Concentration, g/L	Total salinity
NaCl	4.46	
NaHCO ₃	0.29	
CaSO ₄ *2H ₂ O	2.63	8.56
MgSO ₄ *7H ₂ O	2.09	
Na ₂ SO ₄	0.74	

2.2. Estimation of corrosion resistance under cyclic wetting

Tests with cyclic wetting were carried out on flat-plate specimens 50x30x5 mm in size, cut from 09Mn2Si low-alloy pipe steel used in pile-supported bridges. The potential effect of damage to the protective paint coating on the corrosion rate of steel was tested in specimens with various simulated damages and an undamaged paint coating applied to only one side of the specimen (2), specimens with a coating damage area of ~60 mm² (3), specimens with a coating damage area of ~ 150mm² (4) (Fig. 3).

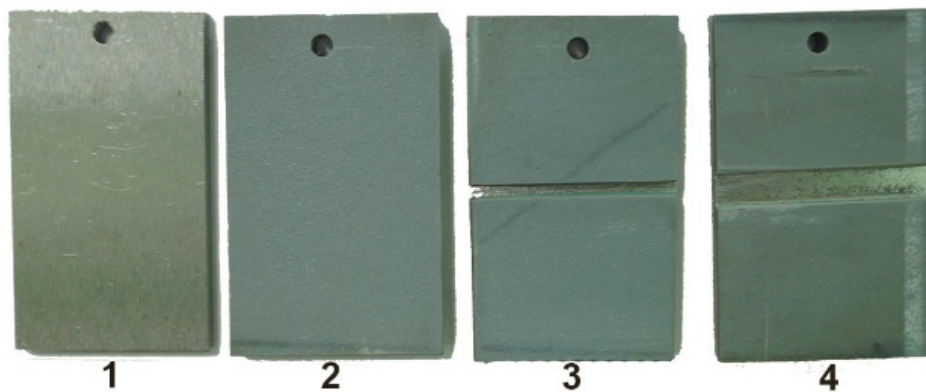


Figure 3. Specimens before testing: 1, uncoated specimen; 2, specimen with coating on one side; 3, no coating over an area of 60 mm²; 4, no coating over an area of 150 mm².

Unpainted and painted specimens with damaged coatings were subjected to cyclic wetting for 30 days. The solution was replaced every 7 days with a freshly prepared one, so the solution of the components was not controlled. Corrosion products consisting of iron hydroxides, which were formed during the interaction of dissolved oxygen and iron ions, did not affect the aggressiveness of the solution. This is due to the fact that the solution was in an open container of a large volume, and this ensured a constant oxygen content in the solution. After the tests were concluded, the specimens were removed from the test solution and cleaned from corrosion products in accordance with Russian State Standard GOST R 9.907-2007 to determine the weight loss and calculate the corrosion rate.

The corrosion rate was found from the weight loss and recalculated in mm/year. The total corrosion rate was calculated by the formula:

$$V = \Delta m / (S \cdot \tau), \quad (1)$$

where Δm is the weight loss, g; S is the surface area of the sample affected by corrosion, m²; τ is the duration of the test, h.

2.3. Estimation of ice-induced wear

We studied the simulated effect of ice on wear using an electrochemical technique, consisting in measuring the electrochemical potential of a steel surface during and after mechanical cleaning. The electrochemical potential of the specimen was measured using a VERSA potentiostat. An EVL-1M3.1 silver chloride electrode was used as a reference electrode. A VED-06 setup was used to rotate the working electrode. A cylindrical specimen serving as the working electrode was fixed in a coupling. The entire surface of the specimen, with the exception of the end face, which was subjected to abrasive friction, was isolated. The appearance of the setup is shown in Fig. 4.

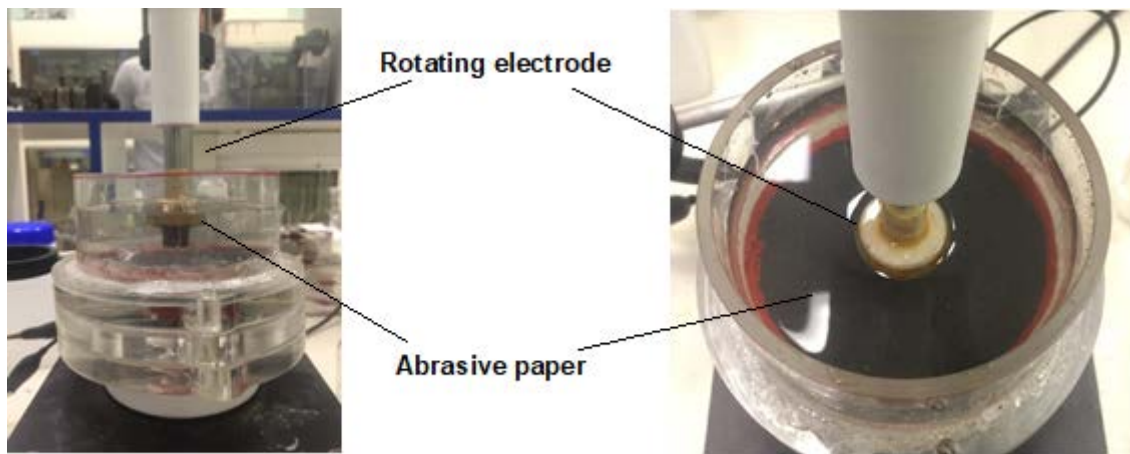


Figure 4.

Appearance of experimental setup.

2.4. Estimation of corrosion resistance in zinc coatings

The specimens for assessing the durability of zinc coatings were plates made of mild steel (St3sp steel) sized 100×50×3 mm with a 120 μm thick hot-dip galvanized (HDG) coating.

Because long-term environmental tests on the coast of the Kerch Strait were not possible, accelerated tests were carried out in a salt spray chamber for 2 months, along with full-scale tests lasting 1 year. In both cases, the corrosion rate of zinc coatings was determined during intermediate examinations of the specimens to estimate the test time required for a constant dissolution rate to be established.

The ratio of the final corrosion rate during tests in a salt spray chamber and in a marine coastal environment can be used to calculate the acceleration factor K . This allows subsequently finding the durability of zinc coatings of any thickness for a given climatic region without long-term environmental tests:

$$T = K \cdot \frac{t}{V_y} \quad (2)$$

$K = V_y/V_a$, where

T is the service life of the zinc coating, years;

K is the acceleration factor;

t is the coating thickness, μm;

V_y is the steady-state corrosion rate of zinc coatings during accelerated tests, μm/year;

V_a is the steady-state corrosion rate of zinc coatings during environmental tests, μm/year;

A more detailed description of the test procedure and metallographic studies of zinc coatings are given in [25]–[28].

3. Results and Discussion

The 09Mn2Si steel specimens were tested under cyclic wetting in a solution with the total salinity of 8.55 g/l (pH 7.4) at room temperature.

Loose reddish brown corrosion products with weak adhesion to the metal were produced during the tests, distributed evenly over the entire surface of unpainted specimens of 09Mn2Si steel. The appearance of the specimens after testing is shown in Fig. 5 (a), the test results are given in Table 3.

As follows from the data obtained, the specimens that were left unpainted had an average corrosion rate of 0.32 mm/year. The specimens which had intact paintwork on one side with the remaining surfaces not isolated from the test solution had an average corrosion rate of 0.30 mm/year. The painted area was not taken into account in the calculations of the corrosion rate.

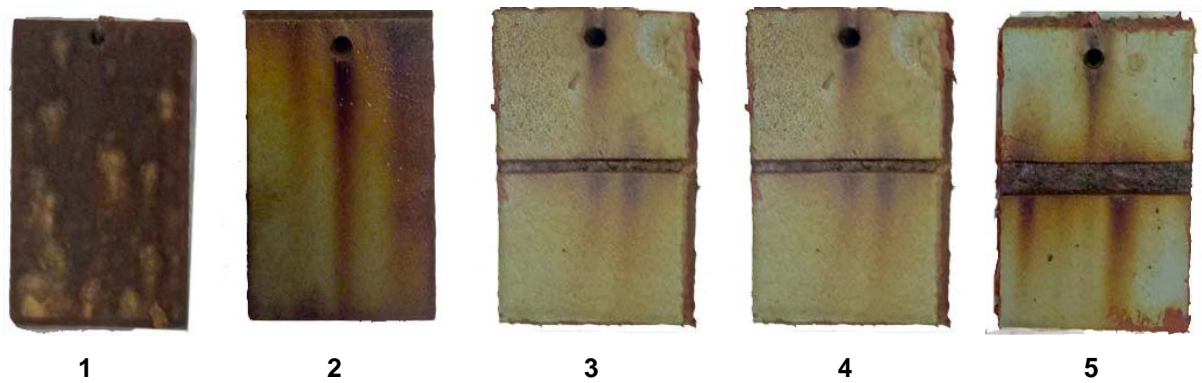


Figure 5. Appearance of specimens after cyclic wetting tests: 1, uncoated specimen; 2, specimen painted on one side; 3, no coating on an area of 60 mm²; 4, no coating on an area of 150 mm².

Table 3. Test results for 09Mn2Si steel specimens at cyclic wetting.

No Specimen	Coating	Corrosion rate, g/m ² *h	Corrosion rate, mm/year	Average corrosion rate, mm/year
1-1		0.3034	0.3198	
1-2	Uncoated specimens	0.3056	0.3236	0.32
1-3		0.3041	0.3211	
2-1		Specimens coated on one side	0.2745	
2-2	0.2606		0.2909	
3-1	No coating over area of 60mm ²	0.2630	0.2935	0.31
3-2		0.2988	0.3335	
3-3		0.2819	0.3147	
4-1	No coating over area of 150 mm ²	0.3072	0.3429	0.32
4-2		0.2786	0.3109	
4-3		0.2735	0.3053	

Specimens with the damaged coating area of 60 mm² and 150 mm² had an average corrosion rate of 0.31 mm/year and 0.32 mm/year. Thus, comparative tests revealed that the presence of mechanical damage to the paintwork does not lead to increased corrosion rates regardless of the area of damage. The corrosion rate of all specimens considered was in the range of 0.30–0.32 mm/year, that is, practically the same. It should be noted that a similar tendency for an increase in the corrosion rate in the zone of variable wetting was shown during the survey of stationary offshore platforms on the shelf of the Black Sea and steel pipes of the pier trestle in the Kola Bay [26, 27].

We experimentally studied the effect of short-term mechanical cleaning of the steel surface during friction against a solid, simulating corrosion-abrasive wear, on the corrosion rate. The experiments consisted in measuring the change in the electrochemical potential during cleaning of the steel surface. We discovered (Fig. 6) that the potential shifts abruptly to negative values from -505 mV to -620 mV from the onset of friction (section 2). This means that the potential difference between cleaned and uncleaned metal surfaces is more than 100 mV. With this potential shift, the corrosion rate of steel increases by more than an order of magnitude. As the friction stops, the potential of the specimen returns to its steady-state value in approximately 17 seconds (section 3). Sections 1 and 4 in Fig. 6 show the electrochemical potential of the specimen in solution before friction started and after it stopped.

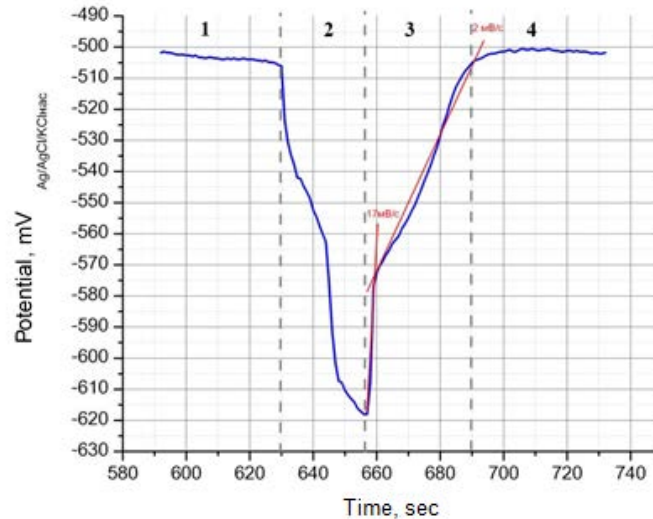


Figure 6. Variation of electrochemical potential of 09Mn2Si steel during friction against a solid.

The total duration of the period when the specimen surface reaches the steady-state electrochemical potential is ~30 s. The data obtained indicate that the metal spends no more than 30 seconds in an active state in a corrosive environment during friction against another solid. A thin oxide film is restored in that time on the surface after friction stops (section 4 in Fig. 6), and the metal potential acquires a steady state when the corrosion rate does not exceed 0.32 mm/year even in the zone with cyclic wetting in the solution whose composition reproduces the seawater in the Kerch Strait. This is a very short period (30 seconds is $\sim 2.5 \cdot 10^{-7}$ of one year), so even assuming that the corrosion rate in the cleaned area increases by 100 times, this metal in this area is expected to thin out by $8.75 \cdot 10^{-6}$ mm ($0.35 \text{ mm/year} \times 100 \times 2.5 \cdot 10^{-7} = 8.75 \cdot 10^{-6} \text{ mm}$) per year. If contact with ice or other solid object at the same point on the surface is repeated 1000 times (which is statistically unlikely), the annual wear of the metal will not increase by more than 10 μm even in this case.

The zinc coatings were measured by a method relying on analysis and processing of the durability data obtained in accelerated tests in the salt spray chamber (Fig. 7) and climatic environmental tests carried out at the coast of the Kerch Strait for 1 year (Fig. 8).

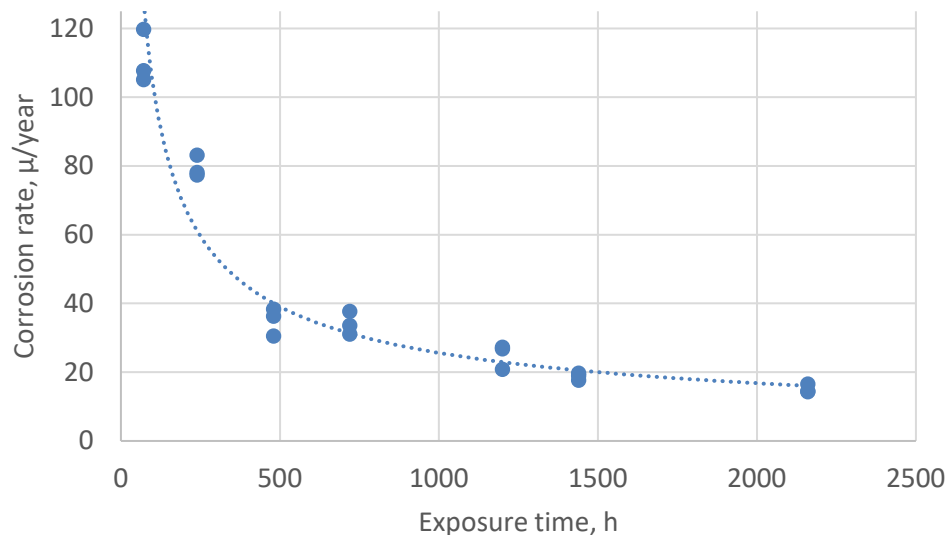


Figure 7. Specimen exposure times in the salt spray chamber versus corrosion rates of zinc coatings.

It is evident from the results obtained in the SST that the corrosion rate decreases from 120 $\mu\text{m}/\text{year}$ to 19 $\mu\text{m}/\text{year}$ upon exposure from 72 to 1440 h, respectively, slightly decreases to 15–17 $\mu\text{m}/\text{year}$ and an increase in exposure to 2280 h, remaining practically unchanged. A possible explanation for this is that

corrosion products form, preventing the corrosive environment from reaching the coating and thus slowing down the dissolution of the zinc coating. Therefore, we can assume that the corrosion rate of zinc coatings takes on a constant value equal to 15–20 $\mu\text{m}/\text{year}$ after accelerated tests lasting about two months.

The corrosion rates established in full-scale tests of the specimens for HDG zinc coatings are shown in Fig. 8. The experiment and results are described in detail in [28].

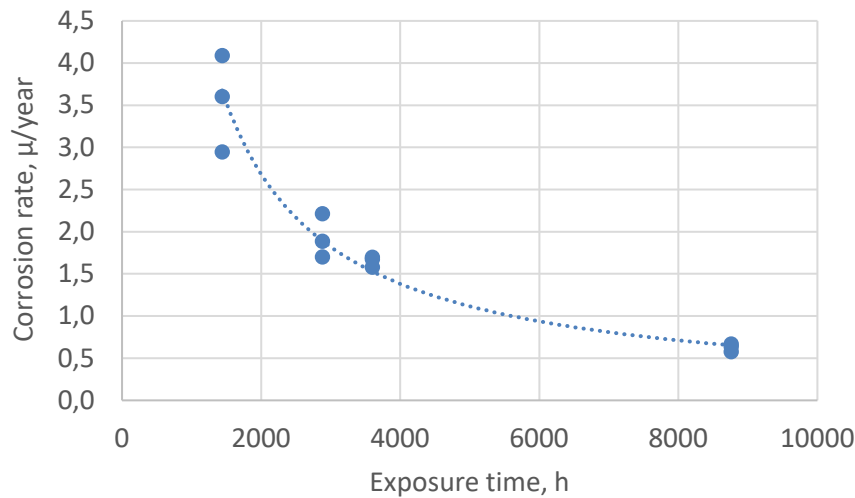


Figure 8. Specimen exposure times in marine environment versus corrosion rates of zinc coatings.

The results of full-scale tests confirm that the corrosion rate of HDG zinc coatings falls from 3.54 $\mu\text{m}/\text{year}$ to 0.63 $\mu\text{m}/\text{year}$ upon exposure from 1440 to 8760 h, respectively. Moreover, a significant drop in the corrosion rate is observed in the first half of the test period, subsequently varying within 1.5 $\mu\text{m}/\text{year}$ (from 1.89 $\mu\text{m}/\text{year}$ to 0.63 $\mu\text{m}/\text{year}$). This means that corrosion processes attenuate during full-scale tests as well as during laboratory tests, which may be due to the protective effect of the resulting zinc corrosion products. The HDG zinc coatings could have been exposed to seasonal changes during 1-year-long climatic tests in the Kerch Strait area.

Assuming that the corrosion rate of zinc coatings has stabilized to 15 $\mu\text{m}/\text{year}$ during tests in the salt spray chamber, the acceleration factor K amounts to ~ 7.9 . Given the steady-state corrosion rate in the accelerated tests, the obtained acceleration factor can be used to find the durability of zinc coatings of any thickness, produced by a different technology, for a given climatic region without long-term environmental tests.

Therefore, it seems reasonable to take the steady-state corrosion rate in climatic tests as equal to 1.9 $\mu\text{m}/\text{year}$ for durability calculations of the zinc coating and the acceleration factor K . In this case, the service life of a 120 μm thick coating will amount to about 63 years.

4. Conclusions

1. We have found that the reliability of steel structures exposed to different impacts in the marine environment can be assessed by designing and conducting various types of tests that simulate individual or combined factors in a specific location: corrosive effect of the environment, effect of climatic factors, mechanical effect in a corrosive environment, effect of emerging defects, etc.

2. The tests performed for the 09Mn2Si pipe steel used for a pile-supported bridge in the Kerch Strait have revealed that the corrosion rate in the cyclic wetting zone, which is the most susceptible to corrosion, does not exceed 0.32 mm/year. Mechanical damage to the paintwork does not lead to an increase in corrosion rates regardless of the damaged area.

3. Considering the effect of short-term mechanical cleaning of the steel surface, simulating friction against a solid body, on the corrosion rate, we have carried out experiments on measuring the variation in the electrochemical potential during cleaning of the steel surface, establishing that the annual wear of the metal should not increase by more than 10 μm even with repeated exposure.

4. Climatic tests of steel specimens with a zinc coating 120 μm thick at the coast of the Kerch Strait showed that the annual wear of the coatings should not exceed 1.9 μm during long-term service. In this

case, the estimated service life of the hot-dip galvanized zinc coating 120 μm thick is expected to last over 60 years.

5. The tests carried out for zinc specimens in a salt spray chamber made it possible to find the acceleration factor in comparison with climatic tests in a marine environment. The obtained acceleration factor can be used to assess the durability of a zinc coating of any thickness, produced by a different technology, for a given climatic region without long-term environmental tests.

5. Acknowledgement

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