Influence of full-scale climatic tests on the properties of aluminum alloys in zones of river and marine water mixture

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Abstract. Within nine months, comprehensive studies were conducted on the effect of full-scale climatic tests on the properties of samples of aluminum alloy AMg6 when fully submerged in the estuary region of the Don River (the basin of the Sea of Azov) at two stations. The features of the formation of micro- and macro-fouling communities on experimental plates at one, three, six and nine months after the start of the experiment are shown. It is shown that microfouling communities on the experimental plates begin to form within a month of exposure. Diatoms were the background-forming species during the entire practical period of the study. Single macrozoobenthos organisms begin to appear on the samples after three months and only at second station. After six months, macro-fouling organisms are fixed on plates at both stations. As the exposure period increases, the number and biomass of macro-foulers increases. The corrosion resistance assessment of the samples revealed the absence of intercrystalline corrosion during the entire test period in water, at both stations, as well as pitting corrosion during the first six months of exposure.

1. Introduction
Corrosion processes are irreversible, and therefore, they must be identified at early stages, quantified corrosion damage, and predicted the danger of development in the absence of measures for anticorrosion protection. Economic calculations show that preventing damage, accidents and disasters is much cheaper than eliminating them [1]. Attention to monitoring of the state of structures and prediction the corrosion resistance of materials is paid all over the world. In the aquatic environment, fouling, corrosion, aging and biodeterioration of materials and structures can hinder their operation, up to its complete impossibility [2]. Therefore, the search for solutions to improve the corrosion resistance of metals is of scientific and practical interest.

On apply scale in the national economy, one of the most commonly used metals are aluminum and its alloys, which are easily deformed and are highly processability. From the kinetics of corrosion processes prospective, aluminum alloys are a short-circuited system of multi-electrode elements [3]. Experts pay close attention to the study of the corrosion resistance of the AMg6 alloy, which is in demand in ship and rail car building, aerospace and construction industry. There are some research data of identification of the biological and corrosion resistance of this alloy during both full-scale and
accelerated tests in the marine environment [4–6]. Studies of the corrosion resistance of aluminum alloys have not previously been carried out in estuaries, therefore the purpose of this experiment was to study the combined effect of climatic and biological factors on experimental plates made of AMg6 aluminum alloy in zones of river and marine water mixture.

2. Material and methods
December 19, 2018 the stands with experimental plates of 15×15 cm in area, 2 mm thick made of AMg6 aluminum alloy were installed at a depth of 2 meters on the SSC RAS testing ranges (Coastal scientific expeditionary base “Kagal’nik” (Station 1, St. 1) and hydrometeorological post “Donskoy” (Station 2, St. 2)) at the mouth area of the River Don in zones of river and marine water mixture (figure 1). Uninstalling of plates was partial carried out after one, three, six and nine month exposure in water respectively. Each plate was photographed from both sides, placed in a separate container with water, within 10-15 minutes was delivered to the laboratory at the coastal base for visual inspection and sampling of the outgrowth. The selection and treatment of sessile microbiota was carried out in accordance with standard hydrobiological methods [7].

![Figure 1. The map-diagram of the area of research](image)

The study of the surface microstructure and determination of the local chemical composition of corrosion products was carried out in 2 stages. At first stage of the study (before the experiments even started), the quality of the experimental plates was monitored for the content of third-party components. The measurement results showed that the used aluminum alloy AMg6 meet state standards and do not contain impurities. The second stage was elementary analysis of experimental plates, which was carried out on a scanning electron microscope Carl Zeiss EVO 40 (EHT = 20 kV, I = 1 nA) with an X-ray attachment for energy dispersive microanalysis INCA at a magnification of x400. Calibration of the current value was carried out on a reference sample of cobalt. Spectrum accumulation time 50 seconds.

Determination of hardness was carried out according to ASTM E2546-15 by the Vickers method. Hardness was determined with a Vickers diamond pyramid, at a force of 100 N and a loading rate of 0.5 mm/s.

3. Results and discussion
The hydrochemical conditions of the water area where the experiment was carried out were determined by the interaction of river and sea factors in the formation of the hydrological-hydrochemical regime. The ionic composition of water at Station 1 is predominantly of the sulphate class of the calcium group. The exceptions are cases of increased underground feeding of the Don
Delta branches and the inflow of the Kagal'nik River in conditions of stable stratification in winter. At this time, the water of this area belongs to the sulfate class of the sodium group [8]. Station 2 recorded water of the bicarbonate class of the calcium group. In addition, the surface water layer at both stations was well aerated. It is known that parts of ships and hydraulic structures moving in aerated seawater, in addition to being directly corroded by seawater, are also subject to erosion and cavitation [5]. Apart from hydrological and hydrochemical conditions, the sessile microbiota influence to the immersed in natural reservoirs materials.

Thru the experiment, it was revealed that the colonization of the samples begins with the formation of microfouling communities represented mainly by diatoms. The number of species recorded in microfouling is varied from 23 to 36 at St. 1 and from 18 to 32 at St. 2 (table 1). After a month of exposure, the most common representatives of the species were Bacillariophyta. Biomass and abundance of microphytoperiphyton on the AMg6 plates were 0.2 μg/cm² and 67 cell/cm² respectively at St. 1, number of species – 25; while 0.2 μg/cm² and 53 cell/cm² respectively at St. 2.

**Table 1.** Number of species of microphytoperiphyton on experimental plates at stations.

| Station       | 1 month | 3 months | 6 months | 9 months |
|---------------|---------|----------|----------|----------|
| Kagal'nik (St. 1) | 25      | 27       | 23       | 36       |
| Donskoy (St. 2) | 18      | 23       | 26       | 32       |

![Figure 2. Dynamics of total density of microphytoperiphyton on experimental plates after 1, 3, 6 and 9 months of exposition.](image)

Three months later, diatoms continued to dominate on the AMg6 plates. Their quantitative indicators, such as frequency of occurrence, number of species (27 at St. 1 and 23 at St. 2), abundance (1150 cells/cm² at St. 1 and 712 cells/cm² at St. 2) and biomass (2.2 μg/cm² at St. 1 and 1.6 μg/cm² at St. 2) have significantly increased.

After six months, at both stations a sharp decrease in the abundance to 44 and 66 cell/cm² and biomass of 0.1 and 0.2 μg/cm² was noted on the plates, while the dominance was retained by diatoms. The species composition of phytoperiphyton has changed. There was a relative decrease in the abundance of attached diatoms, which is probably caused by the action of the intense pressure of phytophages. The number of species on the plates has decreased. The species list was supplemented by planktonic algae from the Chlorophyta type.

After nine months of exposure of the plates an increase in the species diversity of microalgae from five types was noted in the development of phytoperiphyton (up to 36 at St. 1 and up to 32 spices at St. 2). Biomass values decreased to 0.0001 μg/cm² at St. 1 while to 0.0003 μg/cm² at St. 2. At the same time, the values of the number increased to 106 cell/cm² at St. 1 while to 139 cell/cm² at St. 2. The
basis of the biomass was composed of a few large-celled diatoms, the abundance of small-celled representatives of the Chlorophyta and Cyanobacteria types.

A macro-fouling community begins to form on the experimental plates after 3 months of exposure. Single individuals of *Tubifex tubifex* (O. F. Müller, 1774) noted at plates exhibited at St. 2 (table 2, figure 3). Their number reached 89 ind/m², 0,04 g/m². Macroinvertebrates appeared at St. 1 after six months of exposure. Molluscs *Dreissena polymorpha* (Pallas, 1771) and *Fredericella sultana* (Blumenbach 1779) formed the basis of abundance and biomass. Its total number was 1019 ind/m², while total biomass was 97,4 g/m². After six months of exposure at St. 2, in addition to *D. polymorpha* and *F. sultana* the crustaceans of *Corophium volutator* (Pallas, 1766), which form specific corofiid silts in the Don Delta, were a mass species. Its total number was reached 8417 ind/m² while total biomass was 156,4 g/m².

**Table 2.** Number of species of macrozoobenthos on experimental plates at stations.

| Station       | 1 month | 3 months | 6 months | 9 months |
|---------------|---------|----------|----------|----------|
| Kagal'snik (St. 1) | -       | -        | 4        | 4        |
| Donskoy (St. 2)   | -       | 1        | 6        | 4        |

![Figure 3](image)

**Figure 3.** Dynamics of total density of macrozoobenthos on experimental plates after 1, 3, 6 and 9 months of exposition.

After nine months, four taxa of macroinvertebrates were recorded on the plates. *D. polymorpha* formed the basis of fouling communities at both St. 1 and St. 2. The total number and biomass were 6116 ind/m² and 161,6 g/m² respectively at St. 1, while 19888 ind/m² and 312,88 g/m² respectively at St. 2.

It should be noted that the population at St. 2 was 3-7 times higher than at St. 1 (figure 3). A similar picture was observed for biomass.

The assessment of the effect of a combination of abiotic and biotic factors on corrosion processes occurring in a natural reservoir was carried out on the basis of the weight loss of metal plates (corrosion rate), metallographic analysis, and the loss of mechanical properties of the aluminum alloy during tensile tests.

Measurements of the elemental composition of the cleaned areas of the sample surface, performed using energy-dispersive X-ray microanalysis, were of a local nature and were repeated many times. As mentioned earlier, according to the data of the studies carried out before the start of the experiment, it was revealed that the AMg6 sample meets state standards and does not contain impurities (figure 4a). After three months, in addition to the main elements Al and Mg, such elements as O, Si, Mn are noted in the spectrum (figure 4b). After six months Si, O, C, Ca, Na, S, Cl, Fe were identified (figure 4c). On
the samples that were in water for nine months, C, Ca, K, O, Cl, Na, Si, S are found (figure 4d). Silicon, calcium and carbon come from organisms of the fouling community, the rest of the elements are included in the ionic composition of water in the surveyed water area.

Metallographic studies were carried out with an assessment of the depth of intergranular and pitting corrosion, during which it was noted that after three months of exposure to water on the AMg6 alloy samples, no corrosion damage and, accordingly, intergranular corrosion were not detected after tests at both stations. After six months of the experiment, pitting corrosion was detected on the AMg6 alloy samples only after exposure at St. 2, its depth was 0.02 mm, intergranular corrosion was not detected after testing at both stations. Nine months after the start of the research, it was revealed that the largest area of corrosion damage (40 %) for the AMg6 alloy was obtained at St. 2. But the area of corrosion damage does not exceed 10 % of the surface at St. 1. According to the results of metallographic studies, it was found that after nine months of exposure in water at both stations, the depth of pitting corrosion of the samples is 0.07 (St. 1) and 0.022 mm (St. 2) respectively. Also there is no intergranular corrosion.

Table 3. The results of measuring the Vickers hardness of AMg6 samples in the initial state and after 3, 6, 9 months of exposition by stations (HV).

| Exposure conditions | 3 months | 6 months | 9 months |
|---------------------|-----------|----------|----------|
| Initial data        | 91.00     | 91.00    | 91.00    |
| Station 1           | 89.50     | 88.50    | 88.00    |
| Station 2           | 89.25     | 88.25    | 88.00    |
The change in the hardness index after three months of the experiment for the AMg6 samples was 1 % (within the error of the device), while after six and nine months it was 3 %.

As a result, for the AMg6 alloy samples, the absence of intergranular corrosion was revealed throughout the entire testing period in water, at both stations, as well as pitting corrosion during the first six months of exposure. The development of corrosion damage on the samples is uniform. According to the results of determining the composition of corrosion products, all tested samples are dominated by surface oxidation products, elements that make up the salts of the aqueous medium of exposure sites (calcium, potassium, sodium, magnesium), as well as elements of organic origin: spongy particles containing a large amount of silicon, oxygen and calcium and carbon-based fibrous elements (microalgae).

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