

UDC. 620.194

CORROSION OF CARBON STEEL IN THE WATER BASINS OF SHEMKIR AND YENIKEND HYDROELECTRIC POWER PLANTS**H.M. Tahirli¹, S.C. Verdiev¹, S.A. Mammadova¹, D.B. Tagiyev¹, T.I. Shirinov²,
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Received 12.08.2023

Accepted 08.10.2023

Abstract: Using gravimetric and electrochemical research methods, the corrosion-electrochemical behavior of carbon steel grade St3 in Kura river water has been studied. Gravimetric measurements were carried out under operating conditions of the Shemkir and Yenikend hydroelectric power stations for one year. Along with this, the ionic and bacteriological composition, as well as some physicochemical parameters of these waters were established. It revealed that St3 in the Kura water corrodes at a rate of (0.04÷0.05) g/m²•hour, which is characteristic of steel corrosion in fresh waters. In the atmosphere of hydraulic structures, steel corrodes at rather a low rate, i.e. (5÷6)10⁻³ g/m² hour. As a result of biochemical analysis, sulfate-reducing bacteria (SRB) were discovered in these waters, which are a dangerous organism that releases the corrosive substance of H₂S. By taking the anodic and cathodic polarization curves, a quasi-stationary steel corrosion rate was established to be 0.06g/m² h.

Keywords: corrosion, hydraulic structures, carbon steel, polarization curves, SRB, gravimetric measurements.

DOI: 10.32737/2221-8688-2023-4-379-387

Introduction

Waterworks (WW) play an important role in the economy of many countries, especially in those which are rich in water resources. These structures provide industry, agriculture and other sectors of the national economy with cheap electricity, drinking water, etc. These structures play a special role in the extraction of oil and gas in difficult conditions from the depths of the sea. The main material used in the construction of hydraulic structures is carbon steel, as well as aluminum, copper and their various alloys.

As is known, all steels, except for stainless steel, are thermodynamically unstable in electrolytes, which include river and sea waters, and corrode at a fairly high rate.

Particularly high speeds are observed in marine environments, where the concentration of corrosive ions is higher than in river waters. The corrosion behavior of steel structures and equipment in oceanic conditions has been discussed quite widely in the world [1.2] as well as in our scientific publications [3]. However, similar publications on the corrosion resistance of steels in fresh waters have been discussed sporadically [4-6]. Scientific research into the corrosion of steels in river waters in our Republic began quite recently - in 2015 at some hydroelectric power stations, namely the Mingachevir and Varvar hydroelectric power stations, as well as the Upper Shirvan Canal, which were built on the Kura River. A similar

study has been carried out at the Bakhrantapa water junction. The results of these studies have been published in [5-6]. But there were and still are other hydroelectric stations in the Republic with fairly high energy indicators. The Shemkir and Yenikend hydroelectric power stations were put into operation in the period of 1987-2000 are among similar structures. These hydroelectric stations are located in the upper pool of the Kura Reservoir and corrosion monitoring has never been carried out there, i.e. the corrosion state of equipment that was

systematically exposed to the corrosive and erosive effects of water, not counting cavitation destruction of the metal, has not been checked [7].

The purpose of this work is to study the corrosion state of above-water and underwater structures by analyzing the corrosion rate of steel in the waters of the above mentioned hydroelectric power stations, using gravimetric and electrochemical measurement methods, as well as physical and chemical analysis of water.

Experimental part

The corrosion rate of steel based on the loss of sample mass was examined under natural conditions, i.e. rectangular steel samples cut from the same steel sheet of St-3 grade with an area $S = (80 \times 25 \times 3 \text{ mm}) 46 \text{ cm}^2$ and secured to a steel frame using a nylon line. The samples were first subjected to mechanical cleaning from corrosion and carbon deposits, then mechanically polished to a shine, and degreased with acetone or ethyl alcohol. After this operation, the steel frames were lowered into water to a depth of 3-4 meters using a reinforced steel rope. The similar operations were carried out for the samples prepared for testing under atmospheric conditions. In this case, the frame with the samples was hung 10-12 meters above the water surface. Taking into account that as a result of corrosion, the mechanical properties of steels can deteriorate, steel rods with a length of 600 mm and a diameter of $(8 \div 10) \text{ mm}$ were also prepared. In a similar manner, they were also secured to a steel frame and lowered into the water. Samples immersed in water from the beginning often, i.e. in 1, 3, 7, 10, 20, 30 days and then every month were removed from the

water, cleaned from corrosion products using a known method, dried with filter paper from moisture, degreased and were brought to the laboratory in a special container to determine the corrosion rate. Samples for atmospheric corrosion tests were removed once a month and treated as above and placed in a container. After a month, the steel rods for mechanical testing were removed from the water, dried and prepared for tensile testing using an Italian-made Matest-24048 device.

Considering that the corrosion of metals strongly depends on the ionic content of electrolytes, the samples of water taken from the place where the steel samples were located had been subjected to physical and chemical analyzes and determined their ionic and, if possible, biochemical composition was established as well. These data are given in Table. 1. It ought to be noted that each time before removing steel samples, water samples were taken from the pool and its pH and temperature was immediately established on site. The corrosion rate of the samples was established using the well-known formula [8-9].

$$K = \frac{m_1 - m_2}{S \cdot \tau}$$

where K - is the corrosion rate,

m_1, m_2 - mass of the sample before testing and after testing, respectively

S - geometric area of the sample,

τ - is the test time.

It has to be kept in mind that these experiments were carried out within one year. In all hydroelectric power plants, in addition to steel, other metals and alloys are used, such as

copper, brass, aluminum, etc. The corrosion resistance of these metals was tested in laboratory conditions under hydrodynamic movement of water. For this purpose,

cylindrical samples with an area $S = 11 \text{ cm}^2$ were made from the above mentioned metals and they were attached to an asynchronous motor and rotated at a speed of 1270 rpm in river water. The corrosion rate of these metals was also determined by mass loss. Electrochemical studies were carried out using a

Dutch-made potentiostat İVIUM-Stat. This device was used to record cathode and anodic curves on steel samples in river waters. Using these curves, it is possible to determine the rate of metal corrosion in current units [9]. In some cases, the composition of corrosion products was determined using the RFA method.

Results and discussion

As noted above, the Shemkir hydroelectric power station has been in operation for 26 years, and the Yenikend hydroelectric power station for approximately 23 years [10]. During this time, the corrosion state of the underwater and surface metal structures of these stations was not systematically studied. The study of the corrosion state of hydraulic structures is also

useful due to the fact that, based on the data obtained, it is possible to predict the service life of these structures.

Table 1 shows the chemical composition, as well as some physical and chemical data of the Kura water taken from the basin of the mentioned above mentioned hydroelectric power stations.

Table 1. Ionic, physicochemical and bacteriological indicators of water taken from the Shemkir and Yenikend hydroelectric power stations

| № | Name of indicator | Unit | Shemkir/Yenikend result | Quality requirements |
|----|--------------------------------|--------------------------|-------------------------|----------------------|
| | | | | QOST 2874-82 |
| 1 | pH | | 8.16 | 6.0-9.0 |
| 2 | Electrical conductivity | $\mu\text{S}/\text{sm}$ | 465/436 | |
| 3 | Carbonate | mq/L | 0/3,60 | |
| 4 | Bicarbonate | mq/L | 144/150 | |
| 5 | calcium (Ca^{2+}) | mq/L | 51.7/51,3 | 250 |
| 6 | Magnesium (Mg^{2+}) | mq/L | 10.7/12,4 | 50 |
| 7 | Ammonium (NH_4^+) | mq/L | 0.13/<0,1 | |
| 8 | Chloride (Cl) | mq/L | 16/17 | <350 |
| 9 | Nitrite (NO_2^-) | mq/L | 0.097/0.11 | |
| 10 | Nitrate (NO_3^-) | mq/L | 4.3/4 | <45 |
| 11 | Sulfate (SO_4^{2-}) | mq/L | 94/92 | <500 |
| 12 | Phosphorus phosphat | mq/L | <0.4/1.06 | |
| 13 | Total coliform bacteria | KYV/100 ml CFU/100 ml | 1.94 | <3(KYV/100 ml) |
| 14 | E.Coli | KYV/100 ml CFU/100 ml | 3 | |
| 15 | Clostridium perfringens | KYV/100 ml CFU/100 ml | 147/7200 | |

As can be seen from the Table, the concentration of corrosive ions such as Cl, SO_4^{2-} , HClO^{3-} is much lower than in ordinary drinking water. These data for both

hydroelectric power stations can be said the same, but the bacteriological composition is different. In our opinion, such a difference in running water is a random. On the other hand,

the distance between these stations is only 17 km and sulfate-reducing bacteria SRB, which, feeding on SO_4^{2-} ions, release H_2S , and this substance is a very corrosive component for many metals and alloys. Over this short period, the concentration of SO_4^{2-} ions cannot change much so that the quantity, or rather the volumetric concentration, of SRP differs so significantly from each other. Of course, these bacteria (SRB) exist in the Kura Reservoir, as our previous reports indicate this [5]. But for now, it is impossible to accurately establish their population in flowing fresh waters and the

dependence of reproduction on various natural factors, since this requires systematic biochemical research for quite a long time.

The results of corrosion experiments are shown in Fig. 1. As can be seen from the Figure, at first the steel naturally corrodes at a high speed, and then after 1.5-2 months the speed stabilizes and corrodes at a constant speed equal to $0.03\text{q/m}^2\cdot\text{hour}$. Under atmospheric conditions, the dependence of the corrosion rate on time is approximately linear, but at the end of the experiment it stabilizes at a rate equal to $(5\div 6)10^{-3}\text{q/m}^2\cdot\text{hour}$.

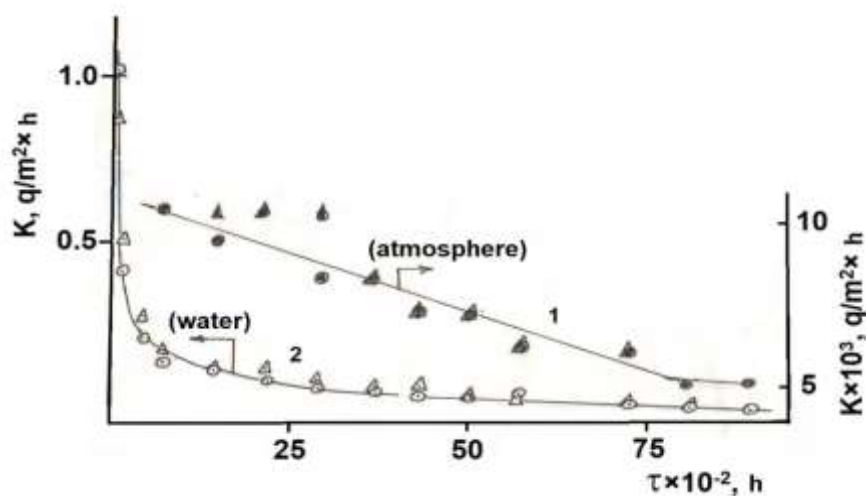


Fig. 1. Dependence of the corrosion rate of St3 on time in the waters of the Shemkir (o) and Yenikend (Δ) hydroelectric power stations and in the atmospheres of the indicated hydroelectric power stations

Fig. 2 shows the results of a tensile test of steel rods after they were corroded in the Kura water. As can be seen from the Figure, during the test

the steel lost its mechanical properties by approximately 17%.

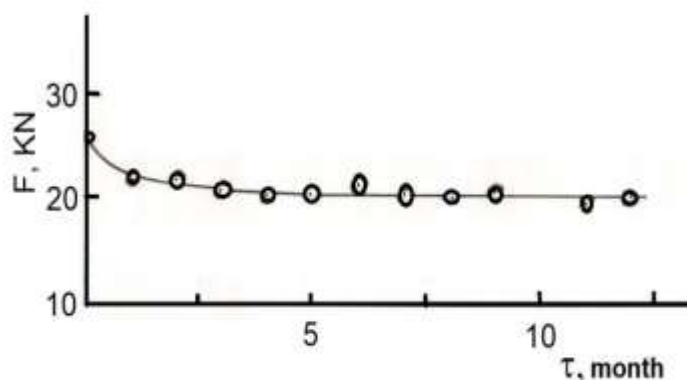


Fig. 2. Dependence of the tensile strength of the steel bar on the time of corrosion testing in the water of the Shemkir hydroelectric station.

During corrosion tests at the Yenikend hydroelectric power station, black corrosion products were revealed on some samples. Typically, the corrosion products of low-alloy steels are brown in color and consist of various oxides and oxohydroxides of iron. Analysis of these corrosion products by X-ray phase analysis (RFA) showed that among the corrosion products, in addition to oxygen compounds, there is also iron sulfide FeS. These data are shown in Fig. 3.

As is known [1.2], waterworks operating in marine conditions are subjected to the corrosive effects of not only aggressive ions and oxygen dissolved in sea water, but also the

action of SRB. The hydrogen sulfide released by these bacteria vigorously interacts with the main component of steel, iron, and intensively destroys these structures in the absence of the necessary protection. As is seen from Tables 1 and 2, the amount of SRB in the Shemkir reservoir is 147 pieces per 100 ml of water, and in the Yenikend reservoir 7200 pieces per 100 ml of water. Perhaps, for this reason, we discovered FeS in corrosion products. It should be immediately noted that in our subsequent tests FeS was not observed and only oxygen compounds of iron were present in the corrosion products.

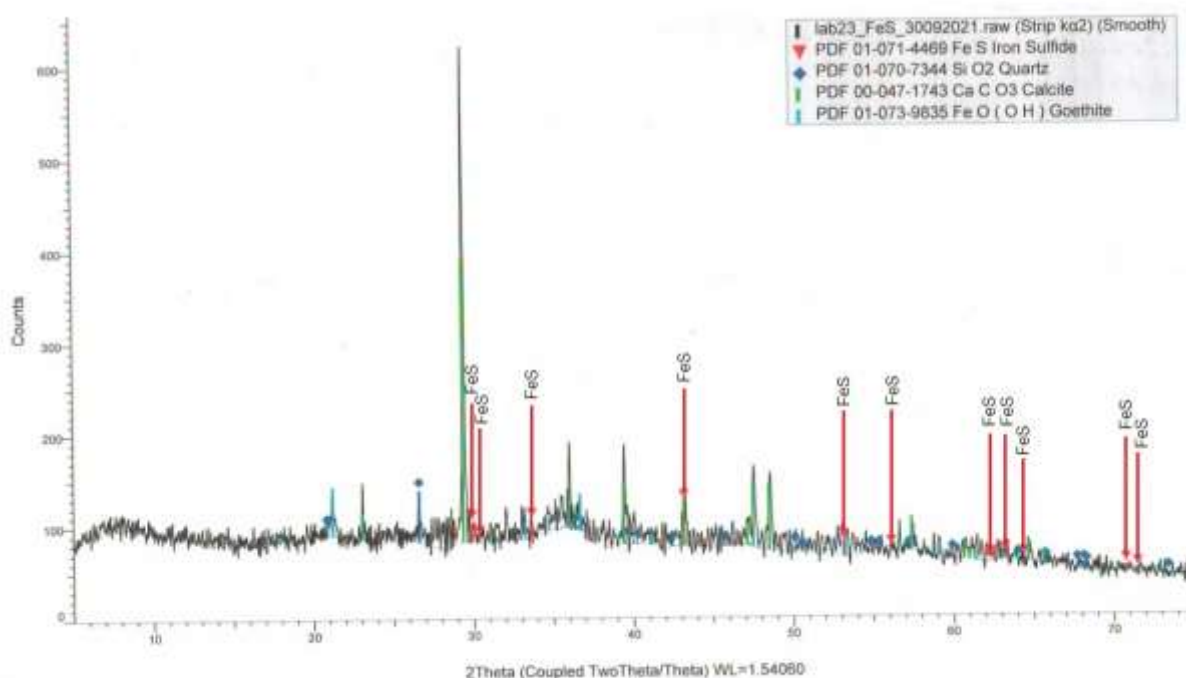


Fig. 3. X-ray diffraction pattern of St3 corrosion products formed on steel in the water of the Yenikend hydroelectric station

In hydraulic structures of any hydroelectric power station, in addition to steel, other metals and alloys are used, such as copper, brass, aluminum and its alloys. Information about the corrosion resistance of these materials in the waters under study is also of no small interest. With that end in view, cylindrical samples were made from these materials and

subjected to corrosion testing under hydrodynamic conditions for 10 days in a laboratory setup, which we noted in the methodological part of this message. Cylindrical samples were made of aluminum alloy D16, brass grade L68 and copper M3. The obtained data are shown in Fig. 4.

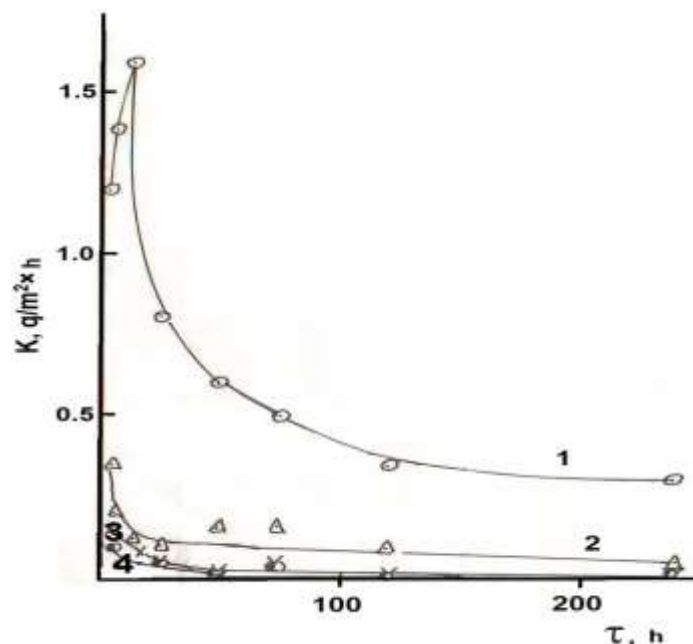


Fig. 4. Dependences of the corrosion rate of St3 (1), aluminum alloy D16 (2), brass L68 (3) and copper M3 (4) on time in the waters of the Shemkir hydroelectric power stations

For comparison, the Fig. 4 shows similar data for St3. Steel in river water first corrodes at a high rate ($\sim 1.6 \text{ g/m}^2 \cdot \text{hour}$), and then gradually decreases and stabilizes. Alloy D16 (cr.2) in comparison corrodes with steel at a low speed and after ~ 10 hours stabilizes and continues to dissolve at a lower speed $(3 \div 4) \cdot 10^{-2} \text{ q/m}^2 \cdot \text{hour}$. Brass and copper corrode at a still low rate $(3 \div 4) \cdot 10^{-2} \text{ q/m}^2 \cdot \text{hour}$. It is possible that with a longer test, the data presented may be even

lower.

Along with corrosion tests, in order to study the corrosivity of the environment, in line with accepted practice, research also studies the electrochemical characteristics of steel in the given environment. Fig.5 shows the cathode and anodic polarization curve of St 3 in the Kura water, taken from the Yenikend hydroelectric station.

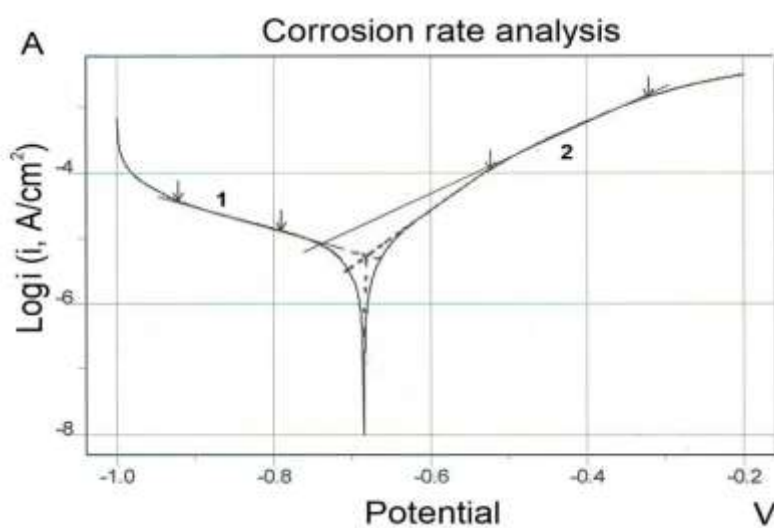
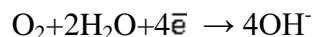


Fig. 5. Cathode (1) and anodic (2) polarization curve of St3 in the water of the Yenikend hydroelectric station

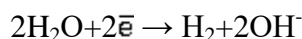
**a correction has been made to the computer version of the slope of the polarization curve*

As can be seen from the Fig. 5, the open circuit potential of steel is $E = -0.680\text{v}$. In the negative region from this potential, as usual, the

reduction of molecular oxygen occurs according to the reaction



And after the potential $E = -0.98\text{ v}$, hydrogen is released according to the reaction



More positive than $E = -0.680\text{v}$, the anodic process of steel dissolution occurs. The intersection of the slope of the Tafel sections near the stationary potential corresponds to the corrosion rate in current units. The corrosion rate of steel in the Kur a water, measured in a

similar way, is equal to $i_{\text{corr}} \approx 6 \cdot 10^{-6} \text{A/cm}^2$. The corrosion rate measured by mass loss (negative mass measurement indicator) K_m ($\text{g/M}^2 \cdot \text{r}$) is related to the current corrosion rate indicator (A/cm^2) by the following dependence [9]:

$$K_m = \frac{i \cdot A}{n \cdot 2.68 \cdot 10^{-3}}$$

where

K_m - negative indicator of corrosion rate, $\text{g/m}^2 \cdot \text{hour}$

i - Corrosion rate in current units, A/cm^2

n - Number of electrons participating in the anodic process

A - Atomic mass of the metal

The corrosion rate calculated using this equation is $K_m = 6.3 \cdot 10^{-2} \text{ g/m}^2 \cdot \text{hour}$. This corrosion rate value, being slightly different from gravimetric

measurements, is the actual corrosion rate in river water [6].

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Encyclopedia Meloration and Water

ŞƏMKİR VƏ YENİKƏND SES-LƏRİNİN SU HÖVZƏLƏRİNDƏ KARBONLU POLADIN KORROZİYASI

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Xülasə: Kür çayı sularında qravimetrik və elektrokimyəvi metodların köməyi ilə karbonlu St3 poladının korroziya elektrokimyəvi xassələri tədqiq olunaraq öyrənilmişdir. Qravimetrik ölçmələr bir müddət Şəmkir və Yenikənd SES-lərin istismarı şəraitində aparılmışdır. Bununla yanaşı suların ion və bakterioloji tərkibi, həmçinin bəzi fiziki-kimyəvi parametrləri öyrənilmişdir. Məlum olmuşdur ki, St3 polad Kür çayı sularında bu tip poladların şirin sular üçün xarakterik olan $(4\div 5)\cdot 10^{-2} \text{q/m}^2\cdot \text{saat}$ sürətlə korroziya məruz qalır. Qeyd olunan sularda biokimyəvi analiz nəticəsində H₂S ifraz edərək poladların korroziya davamlılığı üçün təhlükə yaradan sulfat reduksiyaedici bakteriyalar (SRB) aşkar edilmişdir. Çay suyunda katod və anod əyriləri çəkməklə poladın $0.06 \text{q/m}^2\cdot \text{saat}$ bərabər olan kvazistasionar korroziya sürəti müəyyən edilmişdir. Alınan məlumatlara əsasən, hidrotexniki qurğuların metal konstruksiyalarının xidmət müddətini proqnozlaşdırmaq mümkündür, belə ki, metal ilkin qalınlığının 30% itirdikdə, o özünün konstruksiya qabiliyyətini də itirir.

Açar sözlər: korroziya, hidrotexniki qurğular, karbonlu poladlar, polyarlaşma əyriləri, sulfat reduksiyaedici bakteriyalar, qravimetrik ölçülər.

КОРРОЗИЯ УГЛЕРОДИСТОЙ СТАЛИ В ВОДНЫХ БАССЕЙНАХ ШЕМКИРСКОЙ И ЕНИКЕНДСКОЙ ГЭС

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Аннотация: Гидроэлектростанции (ГЭС) подвергаются разрушению в результате коррозии, эрозии, кавитации и нередко биокоррозии, особенно в морских условиях. В результате длительных (1 год) испытаний, проводимых на Шемкирском и Еникендском ГЭС, было установлено, что углеродистая сталь марки Ст3 подвергается коррозионному разрушению квазистационарно со скоростью $(0.04\div 0.05) \text{г/м}^2\cdot \text{час}$. Во время проведения коррозионных опытов нами были обнаружены в обоих гидротехнических сооружениях сульфат редуцирующие бактерии (СРБ), которые выделяют с точки

зрения коррозии очень опасное вещество H_2S . В атмосферных условиях (в атмосфере ГЭС) сталь корродирует примерно на порядок с низкой скоростью, т.е. $(5\div 6) \cdot 10^{-3} \text{ г/м}^2 \cdot \text{час}$. Кроме коррозионных испытаний нами был установлен ионный состав, а также некоторые физико-химические показатели Куринской речной воды. На основе полученных данных можно прогнозировать срок службы металлических сооружений этих гидротехнических сооружений, исходя из того, что металл при потере первичной толщины на 30% теряет свои конструкционные способности.

Ключевые слова: коррозия, гидротехнические сооружения, углеродистая сталь, поляризационные кривые, СРБ, гравиметрические измерения.