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CORROSION OF CARBON STEEL AND SOME OTHER METALS IN FRESH WATER OF HYDRAULIC STRUCTURES (HS)

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Abstract: Using the method of gravimetric and electrochemical measurements, the corrosion rate of St3 steel in the water basins of the Takhtakerpi and Shemkirchay hydroelectric power stations has been determined. To establish the expected corrosivity of water, the chemical composition and some physicochemical parameters of the above waters have been determined. As a result of long-term measurements carried out over one year, it has established that steel in the water basins of the Takhtakerpi and Shemkirchay hydroelectric power stations corrodes at a rate of 0.04 g/m² h and (0.07÷0.08) g/m² h, respectively. And in the atmosphere of these hydroelectric power plants, steel corrodes at a low rate, approximately an order of magnitude lower. Analysis of water taken from these hydroelectric power stations showed a very low content of corrosive ions, the concentration of which, especially in the Shemkirchay reservoir, corresponds to spring water. By taking polarization curves it has been established that the rate of steel corrosion is controlled by the concentration of dissolved oxygen in water.

Key words: carbon steel, gravimetric measurements, corrosion rate, polarization curves.

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Introduction

The hydraulic structures (HS) of national importance in the territory of the Republic of Azerbaijan are the hydroelectric power plants (HPPs) constructed on the Takhtakorpu and Shamkirchay reservoirs. The first of them provides the nearest areas and settlements (Baku and Sumgait) not only with electricity, but also with drinking water. The primary goals of the second HS are to deliver irrigation water for the large agricultural plains of the Shamkir region and drinking water to the Ganja city and Samukh regions [1]. The uninterrupted and safe

operation of these gas generators is largely determined by the corrosion resistance of metal equipment, which mainly consists of unalloyed carbon steels. In its turn, these steels are thermodynamically unstable in aqueous environments and are subjected to corrosion destruction. In our previous reports, it was noted what consequences and problems are created by the failure of gas equipment as a result of corrosion [2-5]. In addition to colossal material losses as a result of accidents at gas stations, there is a huge irreversible loss of water

resources. Considering that our republic is not rich in natural water resources, such losses are unacceptable for the country. Therefore, as follows from state law No412-11Q of December 27, 2002, to preserve water resources, it is necessary to periodically monitor the corrosion state of metal equipment of public utility systems [4, 6]. It should be noted that the corrosion experiments were carried out for one year, since during this time a constant corrosion

rate was completely established on the steel. On the other hand, the above-mentioned experiments have been carried out under natural conditions and at the same time the experimental conditions, such as temperature, chemical composition, water flow rate, etc., have been periodically changed in a metal-water corrosion system, so the data obtained will most likely be averaged.

Experimental part

The methods used for this study are described in detail in our previous works [2, 7]. It should only be noted that in this case, we have not studied the effect of steel corrosion on its mechanical properties. Physical-chemical indicators of these waters were carried out in the laboratory of the Azersu Open Joint Stock

Company. We carried out some physical and chemical (temperature, pH) measurements regularly and recorded them for one year. The polarization curves were recorded in a three-electrode glass cell using a Dutch-made IVIUM-stat potentiostat.

Results and discussion

It is known that in electrolytes, in the process of metal corrosion, depending on the pH of the environment, in addition to molecular oxygen, hydrogen and hydroxyl ions, anions such as Cl^- , SO_4^{2-} , HCO_3^- , etc. also take part, if this environment does not contain various types of bacteria, including sulfate-reducing bacteria

[8,11]. Based on this, it would be advisable to analyze and establish the ionic composition of these water basins, where St3 carbon steel was exposed to corrosion. It should be recalled that these reservoirs are not polluted by industrial and other waste. These data are shown in Table 1.

Table 1. The ionic composition of studied water basins

№	Indicator name	Unit	Shamkirchay/ Takhtakorpu	Quality requirements
				QOST 2874-82
1	pH		7,67/-	6.0-9.0/-
2	Electrical conductivity	$\mu\text{S}/\text{cm}$	270/-	
3	Total dissolved salts	mq/L	-/192	<1000mg/L
4	Overall hardness	mq/L	-/164	<350 mg/L CaCO_3 (<7mg/ekv L)
5	carbonate	mq/L	0/-	
6	bicarbonate	mq/L	-/91.5	
7	Calcium (Ca^{2+})	mq/L	42.5/22.9	250
8	Magnesium (Mg^{2+})	mq/L	12/7.52	50
9	Ammonium (NH_4^+)	mq/L	<0.1/<0.04	
10	chloride (Cl^-)	mq/L	<4.75/4.28	<350
11	nitrite (NO_2^-)	mq/L	0.20/<0.03	
12	Nitrate (NO_3^-)	mq/L	6.8/2.20	<45
13	Sulfate (SO_4^{2-})	mq/L	25/105	<500
14	Phosphorus (phosphate)	mq/L	1.0-/<0.04	
15	Lithium (Li^+)	mq/L	-/<0.05	

16	Sodium (Na ⁺)	mq/L	-/8.89	
17	Potassium (K ⁺)	mq/L	-/1.60	
18	Fluoride (F ⁻)	mq/L	-/0.17	1.5

In addition to the ionic composition, this table shows the total amount of dissolved salts, total water hardness and other physical-chemical indicators. As you can see, the concentration of aggressive ions, such as Cl⁻, SO₄⁻², in these waters is very low and they practically cannot affect the rate of steel

corrosion. The decisive factor influencing the corrosion rate is molecular oxygen dissolved in water, which is the main depolarizer in neutral environments; in this case, the corrosion rate is almost completely determined by the current of oxygen reduction on the metal surface to OH⁻ ions:

$$i_c = -i_{O_{2d}} = 4FD(CO_2^0/\delta)$$

i_c - corrosion rate in current units (A/cm²), $i_{O_{2d}}$ -diffusion current of molecular oxygen, F-Faraday constant (C/mol), D- diffusion coefficient (cm²/s), CO_2^0 --volume concentration

oxygen (mol/cm³), δ -effective thickness of the diffusion layer (cm).

Figure 1 shows the results of corrosion tests carried out at the Takhtakorpu HPP.

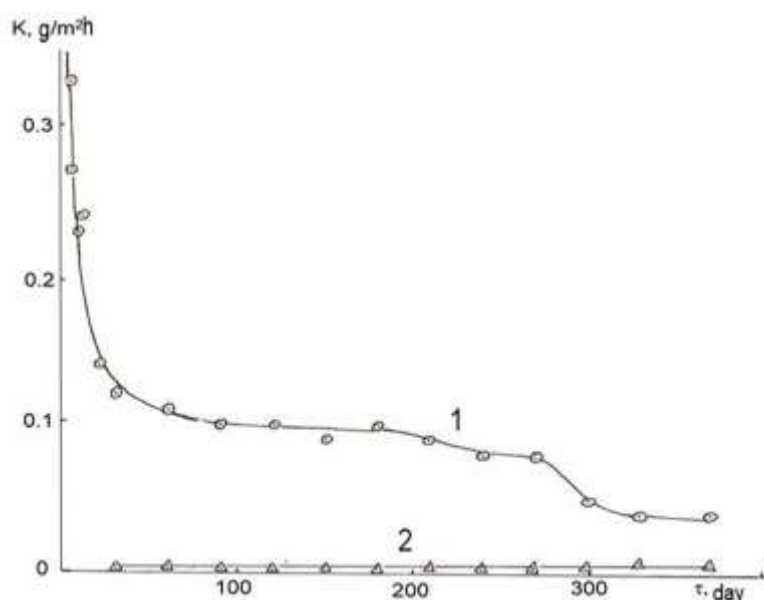


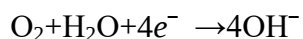
Fig. 1. Dependence of steel corrosion rate on time in the water basin (curve 1) and atmosphere (curve 2) of the Takhtakorpu HPP

It should be reminded that steel samples mounted on a rectangular frame were lowered into water near the water outlet of the generator. As can be seen from the Figure 1 (curve 1), steel first corrodes at a high speed, and then, depending on time, gradually decreases, first reaches a certain plateau and after 200 hours decreases again and reaches its limiting value of 0.04 g/m² h. Under atmospheric conditions, steel corrodes at a rate an order of magnitude lower (4·10⁻³ g/m²·hour), and then increases slightly towards the end of the tests. These corrosion rates, as we noted above, are the

results of tests carried out over a period of one year. To obtain exact and reliable data, longer tests appear to be required because the physical-chemical parameters of water often change depending on the time of year and weather conditions. In addition, each year usually makes its own adjustments to the above water parameters. In this case, the main rate-determining factors of steel corrosion are temperature and saturation of water with molecular oxygen, since the concentrations of corrosive ions in water, are low as we noted above. In summer, when water temperature

risks, the solubility of oxygen decreases, and when it decreases, it increases. When the temperature rises to 800C, the corrosion rate increases, but a further increase leads to a decrease in this value [12]. These data apply to the case where corrosion tests are carried out in an open system. In a closed system, the corrosion rate increases in direct proportion to temperature and has a linear dependence. We assume, that with increasing oxygen content in a weakly concentrated electrolyte (165 mg/kg CaCl_2), the corrosion rate increases linearly. Since there is an opposite relationship between these interdependent quantities, they cancel each other out. With such a complex relationship between the rate of corrosion, temperature and oxygen concentration, nevertheless, dissolved oxygen is the prevailing influence on the rate of corrosion of steel, since its content in the electrolyte depends not only on temperature, but also on the hydrodynamic conditions of water movement. Steel samples,

as we noted above, have been located near the outlet of water from the generator and, as is known, the water is strongly mixed and the solubility of oxygen increases. Thus, steel corrosion under HS operating conditions is almost completely controlled by the reduction of molecular oxygen on the metal surface. Corrosion of steel under atmospheric conditions, i.e. in the operating conditions of a hydroelectric power station has some specificity, namely that it depends on the absolute and relative humidity of the air. In this case, the so-called “dew point”, i.e. this is the temperature at which water vapor, which previously did not saturate the air, becomes saturated at a given temperature. Water vapor condenses on the metal surface and turns into droplets. Oxygen molecules in the air easily diffuse through this thin film of water reach the surface of the metal and are restored according to a well-known formula



In warm weather conditions, the “dew point” is not reached, but in relatively cool and cold weather, this data plays an important role in the corrosion process. It is obvious that the corrosion process occurs in the presence of water and oxygen. A deficiency of one of them reduces it, and an excess accelerates it. Therefore, the corrosion rate of steel in water is higher than in atmospheric conditions.

In addition to steel, other metals and alloys are used in hydroelectric power plants. Figure 2 shows the corrosion rates of steel, D16 aluminum alloy, L68 brass and M3 copper under hydrodynamic conditions. It should be recalled that the movement of the electrolyte was carried out using an asynchronous motor.

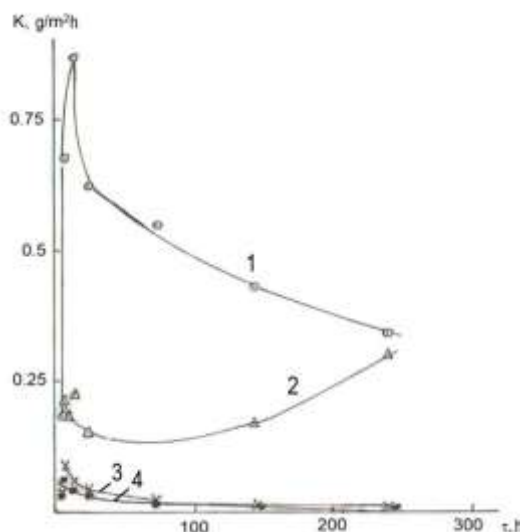


Fig. 2. Corrosion rate of steel (1), aluminum alloy D16 (2), brass grade L68 (3) and copper grade M3 (4), measured under hydrodynamic conditions in water taken from the watershed of the Taktakorpu hydroelectric plant. $V_v=1270$ rpm.

Samples made from the above cylindrical alloys have been rotated in water at a speed of 1270 r/min. As you can see, the steel first corrodes at a high speed, and then naturally decreases to $0.34 \text{ g/m}^2\cdot\text{h}$ within 10 days. Aluminum alloy D16 initially corrodes at a low rate, and then its corrosion rate gradually increases, reaching $0.3 \text{ g/m}^2\cdot\text{h}$ in 10 days. Under these conditions, brass and copper corrode at a low rate equal to $(2\div 3)\cdot 10^{-3} \text{ g/m}^2\cdot\text{h}$. The unexpected high rate of corrosion of D16 is

apparently associated with the high concentration of HCO_3^- ions in the Takhtakorp reservoir, because aluminum and its alloys are unstable in weak alkaline and alkaline environments.

Similar studies carried out in the Takhtakorp reservoir were also carried out in the Shamkirchay reservoir, more precisely in the place where water from the generator flows into the pool. These data are represented in Fig. 3.

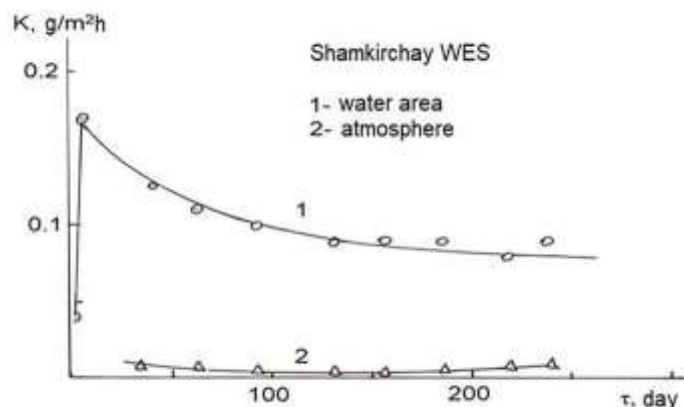


Fig. 3. Dependence of steel corrosion rate on time in water (1) and atmosphere (2) in the waters of the Shamkirchay reservoir.

Let us immediately note that in terms of its physical and chemical indicators, this water corresponds to spring water and is rich in oxygen. The too low concentration of chloride (4.5 mg/l) and sulfate (25 mg/l) ions allows this water to be classified as spring water, and on the other hand, during tests on steel samples, insect larvae from the order *Stenophylax permistus*

were discovered, i.e. the so-called “fontanel” (Fig. 4). According to the staff of the Institute of Zoology of the Academy of Sciences of AR, these insects lay their larvae only in water enriched with oxygen. But we did not find these insects, or rather, their larvae, in other river waters.



Fig. 4. *Stenophylax permistus* larvae deposited on steel

As can be seen from Figure 3 (curve 1), in the first days the steel corrodes at a high speed, then after 100 days it stabilizes and corrodes at a constant and relatively high speed ($0.07\text{--}0.08\text{ g/m}^2\text{ h}$). And in atmospheric conditions, starting from the first days, steel corrodes at a stable low

speed.

Figure 5 shows the dependence of the corrosion rate of various alloys used in HS on the test time under hydrodynamic conditions, similar to the conditions shown in Figure 2.

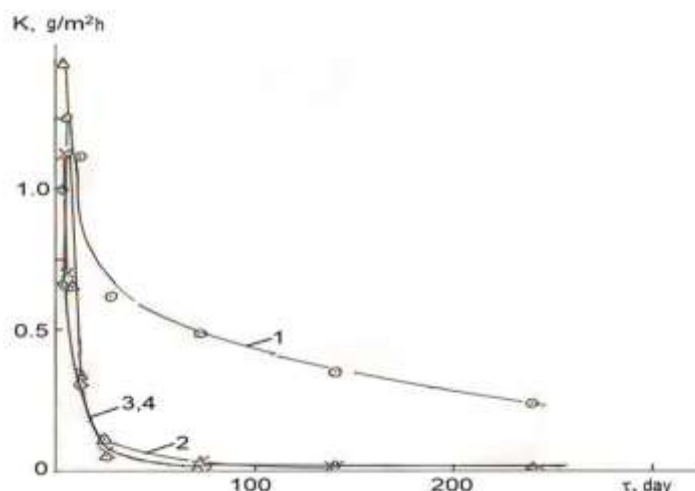


Fig. 5. Dependence of the corrosion rate of steel (1), aluminum (2), brass and copper (3,4) on time in water taken from the reservoir of the Shamkirchay hydroelectric station. The rotation speed of the metal sample is 1270 r /min.

The steel first corrodes at a high rate (curve 1, Fig. 5), and then, decreasing asymptotically, approaches its stationary corrosion rate value. Alloy D16 (curve 2) in this water also corrodes at high speed at first, and

then its speed quickly decreases and corrodes, almost like brass and copper $(5\div6)\cdot 10^{-3}\text{ g/m}^2\cdot\text{hour}$. The reason for this seems to be the chemical composition of the water, as we noted above, which is close to spring water.

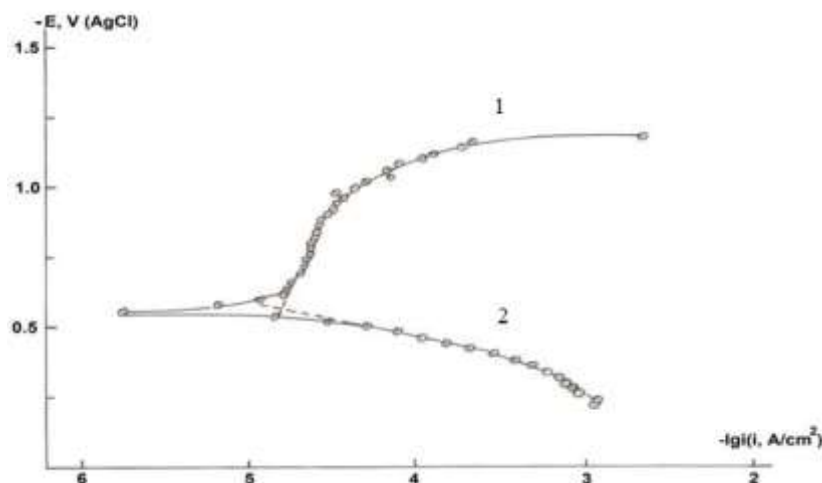


Fig. 6. Cathode (1) and anodic (2) polarization curves of ST3 in Shamkirchay water

By taking polarization curves in the tested aquatic environment, the corrosiveness of river water can be determined. As we noted above, in neutral environments, as well as in weak electrolytes, in which the content of dissolved salts is low, the rate of the corrosion process is determined by the concentration of dissolved

oxygen in the water. Figure 6 shows the polarization curves of carbon steel St 3 in Shamkirchay water. As can be seen from the Figure, the cathode curve clearly shows the region of reduction of molecular oxygen, which occurs at the limiting current. After $E=1.0\text{ V}$, the mechanism of the electrode process changes

sharply and the process of hydrogen evolution from water begins [12]. On the anodic branch of the polarization curve, immediately after the stationary potential, the Tafel section of anodic dissolution of steel begins. Extrapolation of the Tafel sections of the cathode and anodic curves to a stationary potential and the intersection of these curves gives the corrosion rate of steel in the specified environment. The corrosion rate calculated in a similar way in current units is

$i_{\text{corr}} = 1.6 \cdot 10^{-5} \text{ A/sm}^2$, and according to mass loss $K_m^- = 1.67 \cdot 10^{-1} \text{ q/m}^2 \cdot \text{h}$. As you can see, these values are approximately two times higher than the corrosion rates of steel in other aqueous environments [2, 7]. In our opinion, the reason for this is the increased concentration of O_2 in the Shamkirchay reservoir, the composition of which, as we noted above, corresponds to spring water.

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KARBONLU POLADIN VƏ DIGƏR METALLARIN HIDROTEKNIKI QURĞULARIN ŞIRIN SULARINDA KORROZİYASI

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Xülasə: Qravimetrik və elektrokimyəvi metodların köməyi ilə Taxtakörpü və Şəmkirçay su elektrik stansiyalarının (SES) su hövzələrində St3 çeşidli poladın korroziya sürəti ölçülmüşdür. Qeyd olunan suların gözlənilən korrozivliyini yoxlamaq üçün onların kimyəvi tərkibli və bəzi fiziki-kimyəvi parametrləri analiz olunaraq öyrənilmişdir. Bir il müddətində aparılan ölçmələr nəticəsində məlum olmuşdur ki, Taxtakörpü SES-in su hövzəsində polad $0.04\text{q/m}^2\cdot\text{saat}$, Şəmkirçay SES-in uyğun şəraitində isə $(0.07\div 0.08)\text{q/m}^2\cdot\text{saat}$ sürətlə korroziyaya uğrayır. SES-lərin atmosferləri şəraitində isə polad bir tərtib kiçik sürətlə korroziya prosesinə məruz qalır. Bu SES-dən götürülən suların analizi nəticəsində məlum olmuşdur ki, korroziya baxımından aktiv olan ionların qatılığı bu sulara çox aşağıdır və kimyəvi tərkibləri, xüsusilə Şəmkirçay su hövzəsində, bulaq suyuna uyğun gəlir. Qeyd olunan SES-in su hövzəsindən götürülən suda çəkilmiş polyarlaşma əyrilərinin analizi, korroziya prosesinin suda həll olmuş molekulyar oksigenin qatılığı ilə mütənasib olduğunu göstərmişdir.

Açar sözlər: karbonlu polad, qravimetrik ölçmələr, korroziya sürəti, polyarlaşma əyriləri.

КОРРОЗИЯ УГЛЕРОДИСТОЙ СТАЛИ И НЕКОТОРЫХ ДРУГИХ МЕТАЛЛОВ В ПРЕСНЫХ ВОДАХ ГИДРОТЕХНИЧЕСКИХ СООРУЖЕНИЙ

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Резюме: С помощью гравиметрических и электрохимических методов определена скорость коррозии стали марки Ст3 в водоемах Тахтакерпинской и Шамкирчайской ГЭС. С целью проверки ожидаемой коррозионной активности указанных вод был проанализирован и изучен их химический состав и некоторые физико-химические параметры. В результате измерений, проведенных в течение года, установлено, что в водоеме Тахтакерпинской ГЭС сталь корродирует со скоростью $0,04\text{г/м}^2\cdot\text{ч}$, а в соответствующих условиях Шамкирчайской

ГЭС $(0,07 \div 0,08) \text{ г/м}^2 \cdot \text{ч}$. В условиях атмосферы ГЭС стальная конструкция подвергается коррозии с небольшой скоростью. В результате анализа вод, отобранных с этой ГЭС, установлено, что концентрация коррозионно-активных ионов в этих водах очень низкая, а их химический состав соответствует родниковым водам, особенно в Шамкирчайском водохранилище. Анализ поляризационных кривых, построенных в воде, отобранной из водоема указанной ГЭС, показал, что процесс коррозии пропорционален концентрации растворенного в воде молекулярного кислорода.

Ключевые слова: углеродистая сталь, гравиметрические измерения, скорость коррозии, поляризационные кривые.