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CORROSION OF CARBON STEEL ST3 UNDER EXPLOITATION OF HYDROTECHNICAL UTILITIES BUILTS ON THE KURA AND ARAS RIVERS

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There was studied a corrosion of carbon steel St 3 under field conditions of the exploitation of hydrotechnical utilities on the Kura and Aras rivers. Afterlong-term (12 months) experiments we obtained the data confirming that steel corrosion in waters of these rivers occurs by electrochemical mechanism and has cyclic character, that is to say depending on the seasons either increases or decreases. Maximum rate of corrosion under atmospheric conditionsis observed in winter. Such dependence is also observed in aqueous sphere.

***Keywords**: hydrotechnical utilities, corrosion of carbon steel, polarization curves, oxygen and microbiological corrosion*

Hydrotechnical utilities are one of the most metal-consuming fields of national economy. The great role of these utilities in economics of our country is well-known and does not raise doubts. It is enough to remember well-known Oil Rocks, modern oil platforms on Caspian Sea, Mingachevir Hydro Power Plant and other hydrotechnical utilities of different purpose. The main construction materials when building above mentioned utilities are simple carbon steel and iron concrete which are widely used in construction of such objects. Carbon steel is alloy of iron with carbon and thermodynamically unstable in aqueous medium and is exposed to intensive corrosion.As a result of loss of construction the properties of these materials corrosion and due to corrosion accidents may occur, which will lead to catastrophic economic consequences and human losses [1].In our republic systematic studies on corrosive state of marine utilities have been performed by V.F.Negreev and his employees [2]. According to our data, at present such studies are performed in organic scale, materials on study of corrosive state of hydrotechnical utilities in fresh water are absent. We tried to study corrosive state of metal constructions of some hydrotechnical utilities on the Kura and Araz rivers. For this purpose we chose Bakhramtepe hydropower installation in Imishly region, the Upper Shirvan water channel near village Khanabad and tail-bay of Mingachevir Resevoir. Samples for long-term (12 months) of corrosion experiments were cut out (120 pieces) from one of rolled steel plate St 3 with sizes 80×25×3mm. They were first mechanically polished to a mirror finish, degreased with ethyl alcohol and then attached to a special steel frame by capronic grove. These frames with steel samples were sunk into water in above mentioned areas, but similar frames were hung on water surface at a height of 3-4 m with corrosion rate under atmospheric conditions. Corrosion rate of steel was measured gravimetrically by the well-known technique. Samples from corrosion medium were extracted first after 1, 3, 7, 10, 20, 30 days, then periodically after 30 days. First products of corrosion in inhibitor acid were removed from extracted samples, washed off with distilled water, dried and then corrosion rate was calculated by known formula

$$K = (\Delta m)/S \bullet \tau \qquad (1)$$

where K-rate, corrosion g/m^{2}hour, Δ m loss of weight in a time τ, S-sample square in m^2.

Besides gravimetrical measurements for determination of corrosion rate we used electrochemical method – recording polarization curves which allow us to define corrosion rate of metal in current units (A/cm^2).

Polarization measurements were performed in three electrode cell with potentiostat

IVIUM stat, which provides changing electrode potential in wide region with necessary rate. As a comparis on electrode we used silver-chloride electrode of comparison, but as an auxiliary electrode we used platinum wire. In fig.1 we gave dependence of corrosion rate of steel Kontest time under the atmosphere. It should be noted that corrosion tests were begun in July and August. As figure shows,in all curves we observed maximums of corrosion rate and all of them conform to winter months, higher corrosion rates occur relatively at lower temperatures. No matter how paradoxical it was, from chemical kinetics point of view this can be explained.

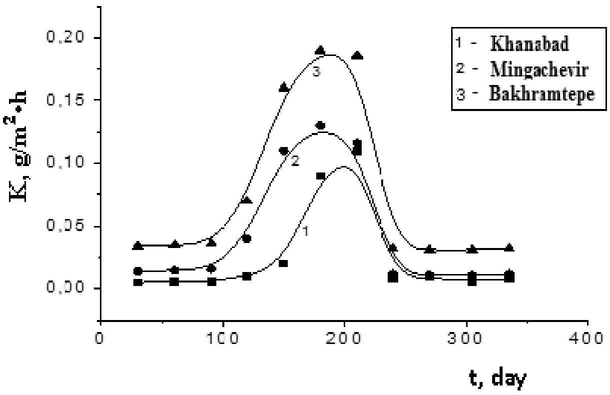


Fig. 1. Dependence of corrosion rate St 3 on testing time in the atmosphere of water resevoirs

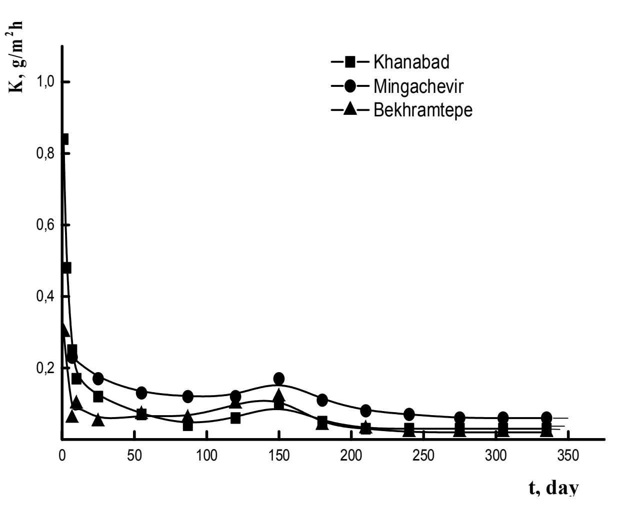


Fig. 2. Dependence of corrosion rate St 3 on testing time in an atmosphere of water medium in different reservoirs

It is well-known that pressure of saturated steam on water depends on the temperature of environment.

At high temperatures evaporation rate increases, but in open space condensation rate decreases, and water steam fails to accumulate on the surface of steel.

Under our conditions corrosion goes exclusively with water and oxygen and at the enough humidity of air, which in its turn depends on temperature, on surface of meal, thin layers of water accumulate and through these layers oxygen diffuse on surface of steel is restored cathodically by the following reaction [3].

$$1/2O_2+H_2O+2e^- \leftrightarrow 2OH^- \qquad (2)$$

Then adsorbed hydroxyl ions enter the reaction with iron atoms of crystalline cell and form FeOH by the reaction

$$Fe+OH^- \rightarrow FeOH(ads)+e^- \qquad (3)$$

$$FeOH(ads) \rightarrow FeOH^+ + e^- \qquad (4)$$

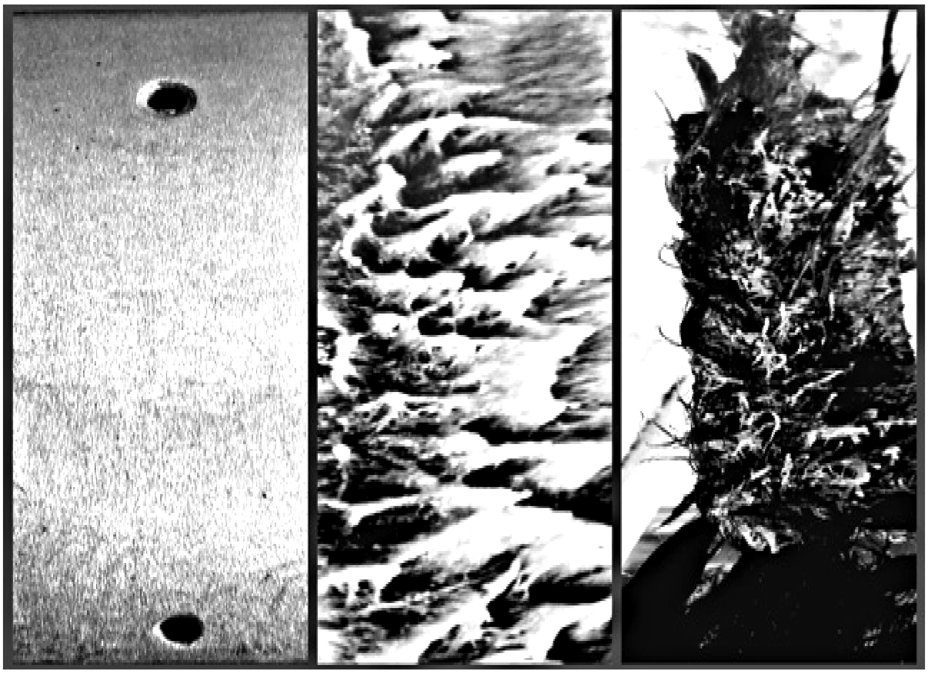
$$FeOH^+ \rightarrow Fe^{2+}+OH^- \qquad (5)$$

As seen from these equations, corrosion of steel proceeds in multi-stage process and products of cathodic reduction of oxygen of OH^-ions play the main role in this case. Thus, at temperatures lower than dew point, the increase of atmospheric corrosion rateis due to accumulation on surface of thin layer of wet, which facilitates corrosion process. Absolute values of corrosion rates of steel in fig. 1 depend on temperature of water, location of samples, direction and power of wind, preliminary processing of steel samples and so on. At high temperature so fair corrosion rate sharply decreases and reaching its limiting value stabilize and are not changed in time. On the basis of obtained data we may suppose that such behavior of steel samples under atmospheric conditions has periodical character and in spring and summer corrosion rate decreases, but in winter and autumn it increases. Unlike laboratorial tests corrosion tests under field conditions are characterized with the fact that terms of experiments periodically change and in this case it is impossible to control temperature, concentration of water sphere, water flow rate, but dependence of rate of corrosion steel on time in aqueous medium follow conventional laws. Though in all reservoirs dynamics of corrosion is different, but as fig. 2 shows steel corrosion in all cases decreases in time and after a certain period stabilizes. In this case on curve at the atmospheric conditions we observed maximums, but these maximums are less well-pronounced. In this case maximums appear in winter. Perhaps, these maximums are quite regular, but not accidental. First of all in all three reservoirs increase of corrosion rate is observed with the decrease of temperature of gas dissolution, as well as oxygen in water increases. At a lower temperature from 20^0 C to 5^0 C dissolution of oxygen in water increases nearly 1,5 time. In neutral solutions corrosion rate is defined by reduction rate of oxygen according to the following equation[3]:

$$i_k = -i_{O_2} = 4FD(C^0_{O_2} / \delta), \qquad (6)$$

where i_k-corrosion rate, i_{O_2} -rate of diffusive limiting current of oxygen reduction, F-Faraday constant, D- diffusion coefficient, C^0_{O2}- concentration of oxygen in electrolyte, δ -thickness of diffusion layer. The symbol minus indicates that i_k- is proportional to negative cathodic current of reduction of oxygen. From equation (6) it follows that corrosion rate i_k depends on concentration of dissolved oxygen. Values D and δ are also functions of temperature [4]. This dependence is complexive and in our case we cannot expect the direct proportionality between rate of steel corrosion and concentration of oxygen. Further, we think that some increase of corrosion rate of steel in winter is an established fact. Distortion of proportionality between i_k and C^0_{O2} can be also related to the formation of different types of depositions on the surface of steel samples. The samples in fig. 3 were sunk into water in tail bay of Mingachevir reservoir.

Huge amount of depositions of plant origin relating to different kind of seaweeds are clearly seen. It should be noted that green seaweeds on surface of samples were formed for a short period, but pale seaweeds were found only after four months in November. To determine origin and biological kind of these depositions they were studied for discovering aerobic saprophytic microorganisms and anaerobic sulfur-reducing bacteria.



a) b) c)

*Fig. 3.*State of surface of steel samples tested in Mingachevir reservoir:
a- initial; b- after 4 months; c- after 11 months

Table

The number of microorganisms detected in water and scrape from metallic samples after exposure in the area of Mingachevir dam in the autumn period

Samples	Microorganisms kl/ml	
	Saprophytic bacteria	Sulfur-reducing bacteria
Water	10^6	10^3
Scrape	10^2	10^7

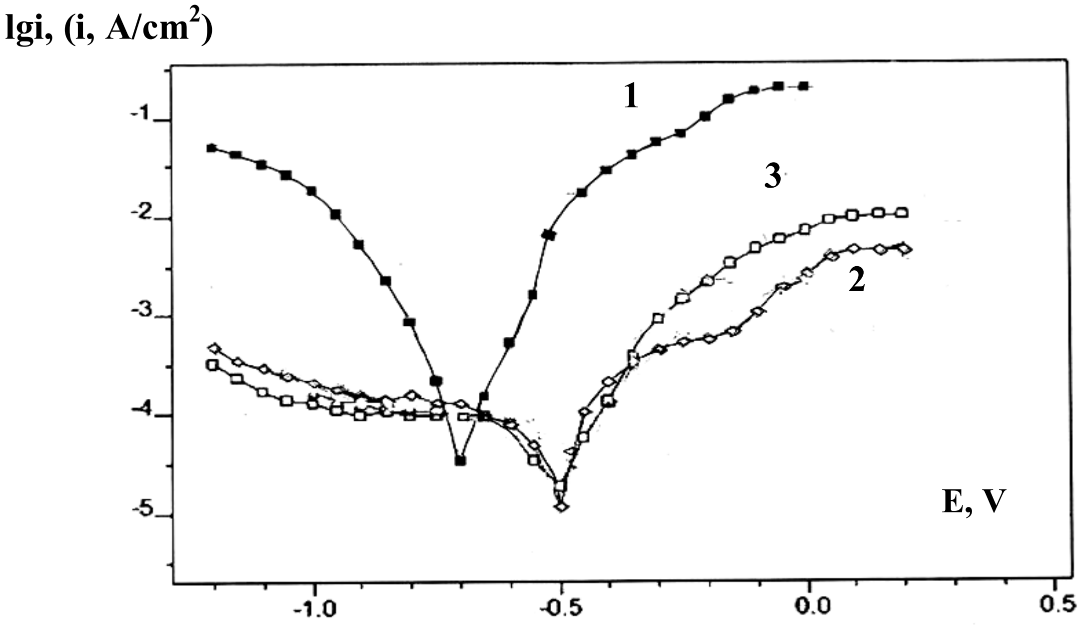


Fig. 4. Polarization curves of steel St 3 in: 1 - 3% NaCl and in river waters; 2 – Kura; 3 – Aras

The results of analysis are shown in table. As seen from the table, the number of saprophytic microorganisms in 1 ml water reaches 10^6, but the number of sulfur-reducing bacteria does not exceed 10^3. In scrape of metal samples the number of saprophytic microorganisms considerably decreases and makes 10^2. Number of sulfur-reducing bacteria increases up to 10^7, due to the fact that aerobic seaweeds intensively absorb oxygen and form favorable conditions for development of anaerobic sulfur-reducing bacteria [5]. As a result, from one hand green seaweeds absorb oxygen and reduce “oxygen corrosion” of metal, from the other hand sulfur-reducing bacteria which develop under these conditions release hydrogen sulfide and facilitates pitting corrosion of steel.

Consequently, activity of corrosive processes on studied area also depends on intensity of development of seaweeds. Perhaps, development of seaweeds in Mingachevir dam has cyclic character, in favorable conditions they develop, then die and this cycle continues, and corrosion processes also have cyclic character and depend on temperature and concentration of oxygen, corrosion rate periodically increases or decreases. As we noted together with gravimetrical measurements we performed polarization measurements for determination of corrosion of reservoirs.

These results were performed in fig.4. For comparison in figure we gave cathodic and anodic curves of steel in 3% solution NaCl.

As seen in fig. 4 in salty solution both curves are mixed to negative direction of potentials and values of current density are considerably higher (by order and more),than curves taken in river waters. Comparison of curves 2 and 3 shows that in the Aras river water values of anodic current are higher than in the Kura waters, which is more mineralized than other rivers of Azerbaijan Republic. It should be noted that water samples for electrochemical measurements were taken near pressure-water pipes from reservoir, where corrosive-aggressive ions of Cl^- and $SO_4^{2-}$and partially HCO_3^- deposit together with solid particles of colloidal solution. This is confirmed by the analysis of water in which amount of SO_4^{2-}in Aras waters is 4,9-5 times higher than in waters taken from Mingachevir reservoir, but amount of Cl^- ions is nearly 6 times higher [6]. Perhaps, certainly this was there as on for higher anodic currents in the Aras waters. Consequently, the higher concentration of these ions in water is the higher dissolution rate of steel in these media. Thus, as follows from above mentioned data, corrosion rate of steel in river waters and atmosphere of the serivers periodically changes depending on temperature of water, its chemical composition and other physical-chemical and microbiological factors of water. It should be noted that in the frame work of this project it is impossible to determine which parameter is the main determining factor of corrosion rate of steel in the river waters. For this purpose it is necessary to perform systematic studies on the effect of physical-chemical and microbiological factors on metal corrosion not only in the Kura and Aras rivers, but also in waters of other reservoirs on which hydrotechnical utilities have been built. In particular, it is necessary to organize all year round observation on change of temperature, chemical composition of main rivers of Azerbaijan Republic in indicated areas.

It is also important to study the effect of different factors (frequencies of electromagnetic radiations, temperature, values of cathodic current and others) on dynamics of development of seaweeds and microorganisms. According to our information such studies either were not performed or these studies are few and are not arranged systematically. Periodical investigations on determination of dissolved oxygen in water should be performed. Due to the separameters these parameters we may create mathematical model of corrosion processes in river waters of Azerbaijan Republic. Only after this the reliable protection of hydrotechnical utilities from corrosion effect of waters can be organize.

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CT 3 CEŞİDLİ KARBONLU POLADIN KÜR VƏ ARAZ ÇAYLARI ÜZƏRİNDƏKİ HİDROTEXNİKİ QURĞULARIN İSTİSMAR ŞƏRAİTİNDƏ KORROZİYASI

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Kür və Araz çayları üzərindəki hidrotexniki qurğuların istismarı şəraitində Cт 3 ceşidli poladın korroziyasının bəzi qanunauyğunluqları tədqiq olunmuşdur. Uzunmüddətli (12 ay) sınaqlar nəticəsində məlum olmuşdur ki, qeyd olunan su hövzələrində poladın korroziyası elektrokimyəvi mexanizm üzrə baş verir və dövri xarakter daşıyır, yəni ilin fəslindən asılı olaraq, ya artır, ya da azalır. Atmosfer şəraitində maksimum korroziya sürəti qış aylarında müşahidə olunur. Uyğun asılılıq su mühitində də baş verir, lakin bu halda müşahidə olunan maksimumlar o qədər də qabarıq ifadə olunmur.

Açar sözlər: *hidrotexniki qurğular, korroziya, karbonlu poladlar, polyarlaşma əyriləri, oksigen və mikrobioloji korroziya*

КОРРОЗИЯ УГЛЕРОДИСТОЙ СТАЛИ МАРКИ СТ 3 В УСЛОВИЯХ ЭКСПЛУАТАЦИИ ГИДРОТЕХНИЧЕСКИХ СООРУЖЕНИЙ, ВОЗВЕДЕННЫХ НА РЕКАХ КУРА И АРАКС

Г.М.Тагирли, С.Ч.Вердиев, К.Ф.Бахшалиева, Д.Б.Тагиев

Была исследована коррозия углеродистой стали марки Ст 3 в натурных условиях эксплуатации гидротехнических сооружений на реках Кура и Аракс. После длительных (12 месяцев) испытаний получены данные, свидетельствующие о том, что коррозия стали в указанных водах протекает по электрохимическому механизму, и имеет циклический характер, то есть, в зависимости от времени года или увеличивается или уменьшается. Максимальная скорость коррозии в атмосферных условиях наблюдается в зимние периоды. Такая же зависимость имеется и в водной среде, но в менее ярко выраженной форме.

Ключевые слова: *гидротехнические сооружения, коррозия, углеродистые стали, поляризационные кривые, кислородная и микробиологическая коррозия*