

# Carbon Steel (St.3) Corrosion Caused by the Circulating Water Flow

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## 1. Introduction

The main factors that define the material corrosion rate in the circulating water are the chemical composition of it, the mineralization, and the amount of dissolved gases, and also the temperature, the pH factor, the metal surface condition and the fluid velocity [1–6]. The latter factor defines directly the running time of industrial equipment, because it is in charge of specific features of the delivery of depolarizer to the metal surface.

The corrosion rate is not a simple function of the flow rate. It also depends on some other factors that have influence on the oxygen diffusion rate. The water flow rate has an essential influence on the corrosion process due to a change in the diffusion layer thickness caused by the formation of a thin layer of corrosion products on the metal surface or by their low density. If the layer of corrosion products has a considerable thickness or high density, then its contribution to the diffusion resistance value is increased to such an extent that the diffusion layer produces no significant influence on the corrosion process.

This statement is very important; because it enables the detection of the mechanism of influence the protective layers have on the diffusion section of pre-electrode layer of the solution. It allows us to establish the reason for the complicated character displayed by the relationship of the corrosion rate of steels with an increase in the flow rate (a decrease in the double layer diffusion section).

## 2. Methods of Experimental Studies

A device with the rotating disk electrode was used to study the influence the circulating water flow rate has on the electrode processes that occur on the carbon steel surface. The studies were carried out using the polished specimens made of carbon steel (St.3) with the diameter  $d = 20$  mm and  $\delta = 3$  mm. The solution temperature was equal to 22 °C, and the pH factor of the solution was checked up every 24 hours and it was adjusted in the case of need. Electrochemical tests were carried out recording polarization relationships using the potentiostat PI-50-1. Platinum was used as an additional electrode. Electrode potentials were measured and compared with those of saturated chloride silver reference electrode and then these were converted to the normal hydrogen electrode scale.

The investigations were carried out for liquid and air contact conditions when the air was passing through the solution or purged through the nitrogen solution. To carry out an experiment we used the circulating water with  $c(\text{NaCl}) = 0.02$  mole·L<sup>-1</sup> and pH = 7 and the circulating water with 0.1 mole·L<sup>-1</sup> and pH = 12. The electrode rotation rate was changed stepwise in the range of 408 to 3930 rp·m<sup>-1</sup>. To convert the linear velocity of the fluid flow in the tube to the equivalent velocity of disk rotation we used the equation [7]:

$$v = 10.3 P_t^{1/4} \sqrt{\frac{2}{R_f} P_l^{1/2} \sqrt{\nu \cdot \omega}} \quad (1)$$

where  $v$  is the linear velocity, m·s<sup>-1</sup>;  $P_t$  and  $P_l$  are the Prandtl numbers for laminar and turbulent fluid flows, accordingly;  $R_f$  is the friction coefficient;  $\nu$  is the kinematic viscosity, cm<sup>2</sup>·c<sup>-1</sup>;  $\omega$  is the disk rotational speed, rp·m<sup>-1</sup>. After substitution of the constants in the equation (1) we obtained the wanted relation (Table 1).

The disk rotational speed was selected to correspond to real velocities of the fluid flow in circulating water supply systems (0.04–0.14 m·s<sup>-1</sup>).

**Table 1.** The relationship between the flow rate in the tube and the disk rotational speed

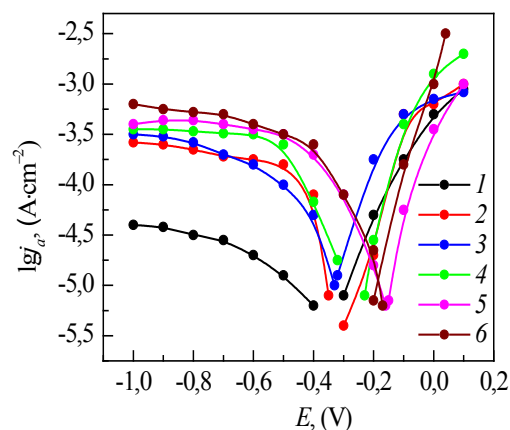
	$v, \text{ m}\cdot\text{s}^{-1}$	$\omega, \text{ rp}\cdot\text{m}^{-1}$
1	0.040	408
2	0.060	840
3	0.085	1500
4	0.118	2880
5	0.140	3930

### 3. Experimental Data

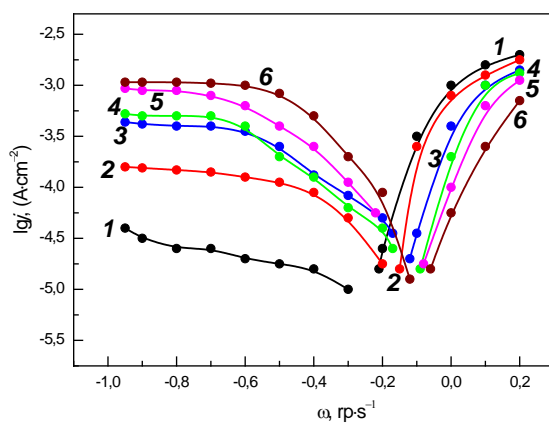
Fig. Fig. 1 to 6 give electrochemical research data. The anode curve shows the passive state domain (Fig. 4, 5) for alkaline solutions when the oxygen is present in the system [8]. For alkaline pH values this domain is observed for all stirring rates and it is reduced with an increase in  $\omega$ . The passive state domain is unavailable on anode polarization curves for neutral pH values (Fig. 1–3), independently of the stirring rate.

The corrosion rate depends to a great extent on the rotational speed. During the rotation with  $408 \text{ rp}\cdot\text{m}^{-1}$  the corrosion current is approximately 2 to 3 times higher in comparison to that in the solution (that was not subjected to) without stirring at  $\text{pH} = 12$  and it is 3 to 5 times higher at  $\text{pH} = 7$ . The passive state domain is reduced significantly during the nitrogen purging of the system. It happens due to the participation of oxygen in the protective film formation [9].

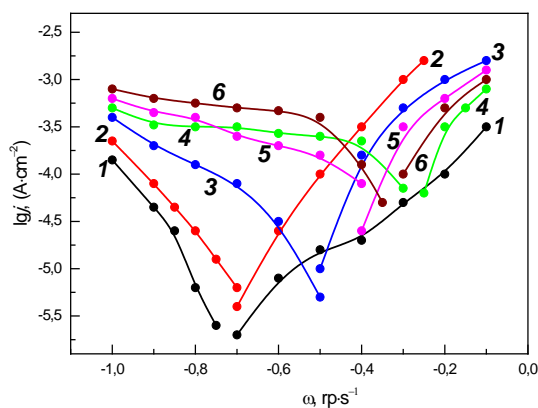
The three domains can provisionally be outlined on cathode polarization curves, in particular, the domain with the electrochemical process defining phase (from  $E$  to  $(-0.5)$ – $(-0.6)$  V), the mixed kinetics domain  $((-0.5)$ – $(-0.7)$  V) and the diffusion kinetics domain  $((-0.6)$ – $(-1.0)$  V).



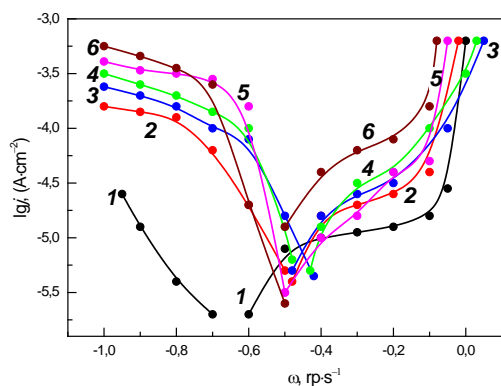
**Fig. 1.** Influence of the rotation frequency of the disk electrode on polarization relationships obtained for the circulating water in the ambient air.  $c(\text{NaCl}) = 0.02 \text{ mole}\cdot\text{L}^{-1}$ ,  $\text{pH} = 7$ .  $\omega$ ,  $\text{rp}\cdot\text{s}^{-1}$ : 1 – 0; 2 – 6.8; 3 – 14; 4 – 25; 5 – 48.3; 6 – 65.5.



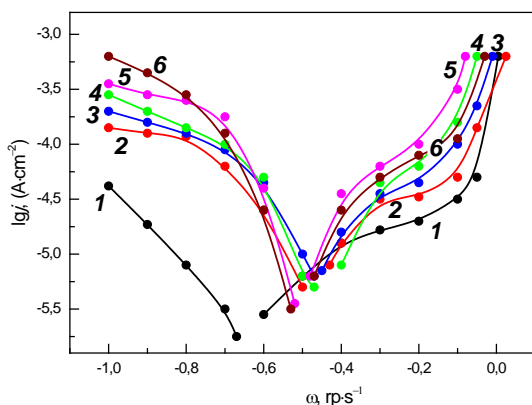
**Fig. 2.** Influence of the rotation frequency of the disk electrode on polarization relationships obtained for the air-purged circulating water.  $c(\text{NaCl}) = 0.02 \text{ mole}\cdot\text{L}^{-1}$ ,  $\text{pH} = 7$ .  $\omega$ ,  $\text{rp}\cdot\text{s}^{-1}$ : 1 – 0; 2 – 6.8; 3 – 14; 4 – 25; 5 – 48.3; 6 – 65.5.



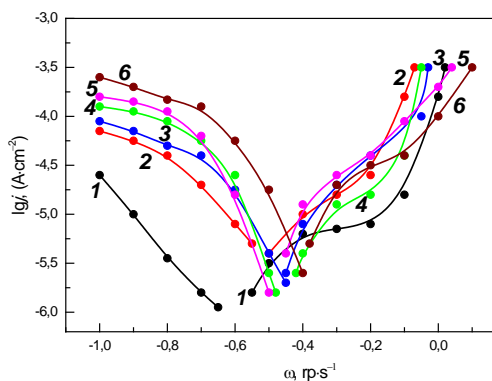
**Fig. 3.** Influence of the rotation frequency of the disk electrode on polarization relationships obtained for the nitrogen-purged circulating water.  $c(\text{NaCl}) = 0.02 \text{ mole}\cdot\text{L}^{-1}$ ,  $\text{pH} = 7$ .  $\omega$ ,  $\text{rp}\cdot\text{s}^{-1}$ : 1 – 0; 2 – 6.8; 3 – 14; 4 – 25; 5 – 48.3; 6 – 65.5.



**Fig. 4.** Influence of the rotation frequency of the disk electrode on polarization relationships obtained for the circulating water in the ambient air.  $c(\text{NaCl}) = 0.1 \text{ mole}\cdot\text{L}^{-1}$ ,  $\text{pH} = 12$ .  $\omega$ ,  $\text{rp}\cdot\text{s}^{-1}$ : 1 – 0; 2 – 6.8; 3 – 14; 4 – 25; 5 – 48.3; 6 – 65.5.

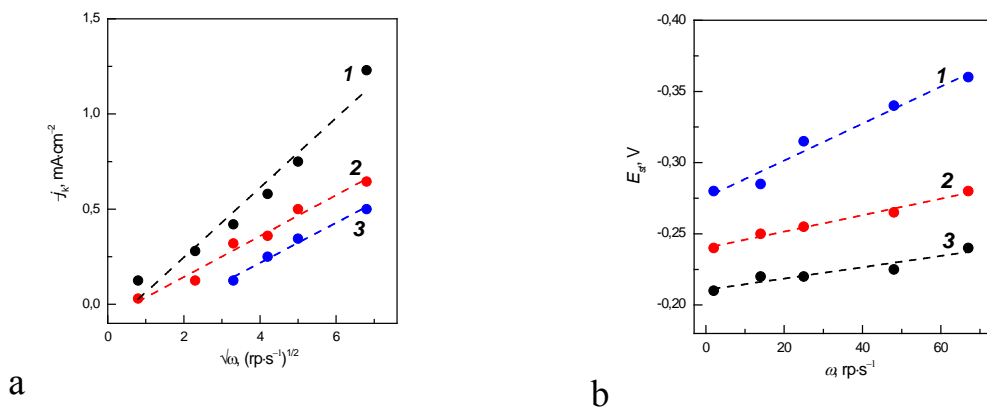


**Fig. 5.** Influence of the rotation frequency of the disk electrode on polarization relationships obtained for the air-purged circulating water.  $c(\text{NaCl}) = 0.1 \text{ mole}\cdot\text{L}^{-1}$ ,  $\text{pH} = 12$ .  $\omega$ ,  $\text{rp}\cdot\text{s}^{-1}$ : 1 – 0; 2 – 6.8; 3 – 14; 4 – 25; 5 – 48.3; 6 – 65.5.

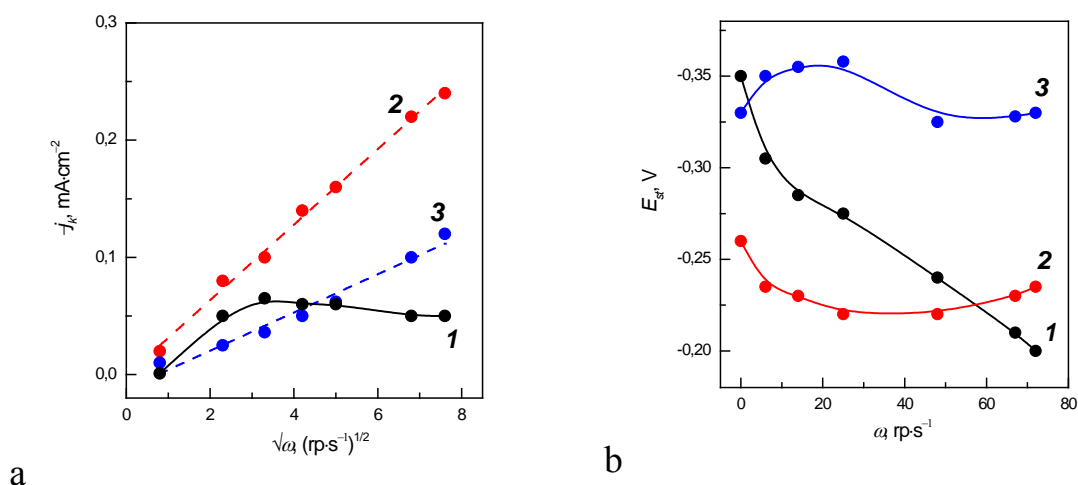


**Fig. 6.** Influence of the rotation frequency of the disk electrode on polarization relationships obtained for the nitrogen-purged circulating water.  $c(\text{NaCl}) = 0.1 \text{ mole}\cdot\text{L}^{-1}$ ,  $\text{pH} = 12$ .  $\omega$ ,  $\text{rp}\cdot\text{s}^{-1}$ : 1 – 0; 2 – 6.8; 3 – 14; 4 – 25; 5 – 48.3; 6 – 65.5.

The potentiometric measurements that were carried out for the polarization potential of  $-0.7$  V (Fig. 7, a; 8, a) showed that the nitrogen purging of the system at  $\text{pH} = 7$  considerably hampers the cathode process (Fig. 7, a, curve 3). This is indicative of that the oxygen supply to the place of reaction is the defining phase for the circulating water at  $\text{pH} = 7$ . The relationship  $j_k = \sqrt{\omega}$  is linear and its angle of slope is defined by the oxygen concentration (Fig. 8, a, the curves 1, 2).



**Fig. 7.** Relationships  $j_k = \sqrt{\omega}$  and  $E_{st} = \omega$  for the circulating water: 1 – air-purged system; 2 – equilibrium with air; 3 – nitrogen-purged system.  $c(\text{NaCl}) = 0.02 \text{ mole}\cdot\text{L}^{-1}$ ,  $\text{pH} = 7$ .



**Fig. 8.** Relationships  $j_k = \sqrt{\omega}$  and  $E_{st} = \omega$  for the circulating water: 1 – air-purged system; 2 – equilibrium with air; 3 – nitrogen-purged system.  $c(\text{NaCl}) = 0.1 \text{ mole}\cdot\text{L}^{-1}$ ,  $\text{pH} = 12$ .

When the system is saturated with the air oxygen and  $\text{pH} = 7$  the cathode process rate is increased (Fig. 7, a, curve 1). This phenomenon is also observed for the working conditions of circulating water supply system when the water is saturated with oxygen in the cooling tower. Saturation of the system with the air oxygen at  $\text{pH} = 12$  results in the deceleration of cathode process (Fig. 8, a, curve 1). The sodium hydroxide develops the properties of the cathode-anode inhibitor at  $\text{pH} = 12$  [8]. The value of cathode current in the solution with  $c(\text{NaCl}) = 0.1 \text{ mole}\cdot\text{L}^{-1}$  and  $\text{pH} = 12$  is 1 to 2 orders of magnitude lower than the value of cathode current in the solution with  $c(\text{NaCl}) = 0.2 \text{ mole}\cdot\text{L}^{-1}$  and  $\text{pH} = 7$ . It is explained by the complicated transfer of oxygen through the protective film formed on the metal and also by a reduced solubility of it (Table 2).

**Table 2.** The influence of pH, temperature and NaCl concentration on the oxygen solubility in the circulating water

$c(\text{NaCl}), \text{g}\cdot\text{L}^{-1}$	$t, ^\circ\text{C}$	pH	$c(\text{O}_2), \text{mg}\cdot\text{L}^{-1}$
1	20–22	7	13.3
1	40–45	7	11.4
1	20–22	12	12.1
10	20–22	7	13.4
10	20–22	12	9.28
10	40–45	12	8.27

The influence the rotating disk has on the value of  $E_{st}$  (Fig. 7, b; 8, b) has been studied. With an increase in the rotational speed the value of  $E_{st}$  shifts to the domain of low values (Fig. 7, b). It confirms the fact that the corrosion rate of circulating water supply systems is increased with an increase in the flow rate at  $\text{pH} = 7$ .

For the solution with  $c(\text{NaCl}) = 0.1 \text{ mole}\cdot\text{L}^{-1}$  and  $\text{pH} = 12$  an increase in the rotational speed of electrode results in the shift of  $E_{st}$  to the positive domain. It is conditioned by the fact that an increase in the stirring rate results in that the cathode process is facilitated to a greater extent and the anode process is facilitated to a lesser extent. Therefore, to preserve the rate equilibrium of anode and cathode reactions the

metal potential is shifted to the positive domain [8, 9]. The corrosion currents in the solution with  $c(\text{NaCl}) = 0.1 \text{ mole}\cdot\text{L}^{-1}$  and  $\text{pH} = 12$  are lower approximately by one order of magnitude than the corrosion currents in the solution with  $c(\text{NaCl}) = 0.2 \text{ mole}\cdot\text{L}^{-1}$  and  $\text{pH} = 7$  at similar electrode rotation velocities.

### 3. Conclusion

It has been established that the carbon steel (St.3) is inclined to the transition into the passive state when the anode is polarized in alkaline solutions.

The passivity is observed in alkaline solutions for all disk rotational speeds and the tendency to the passivation is decreased with an increase in the rotational speed. For neutral solutions, the St.3 steel passive state domain is unavailable for all disk rotational speeds. The nitrogen purging of alkaline solutions results in a considerable reduction of the domain of the passive state of steel and it is explained by a decreased content of oxygen that participates in formation of the protective film. It has been established that an increase of  $\omega$  for the water with  $\text{pH} = 7$  results in the shift of  $E_{st}$  of the steel to the domain of negative values and the corrosion rate is increased.

For the water with  $\text{pH} = 12$ , an increase in  $\omega$  results in the shift of  $E_{st}$  to the domain of positive values and the corrosion rate is decreased. The investigations carried out showed that the water with  $c(\text{NaCl}) = 0.1 \text{ mole}\cdot\text{L}^{-1}$  and  $\text{pH} = 12$  is more acceptable for circulating water supply systems than the water with  $c(\text{NaCl}) = 0.2 \text{ mole}\cdot\text{L}^{-1}$  and  $\text{pH} = 7$  when the flow rate varies in the range of  $0.04$  to  $0.14 \text{ m}\cdot\text{s}^{-1}$ .

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