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Features of influence of some factors corrosion of carbon steel in circulating water

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Summary. The influence of external factors, temperature and flow velocity on the corrosion processes St3 in model solutions petrochemical plant recycled water with high salinity and hardness without open systems and in the presence of the inhibiting composition. It was found that an increase in temperature leads to a linear increase in corrosion rates, and the change in circulating water flow rate leads to the extreme nature of corrosion processes; optimal conditions are determined. Recommended use of cathodic inhibitors or mixed type inhibitor, in particular, the composition "SVOD-BI" (means for controlling the biological corrosion), which can significantly reduce the effect of temperature and flow on the corrosion rate St3, promotes the growth and strengthening of the oxide film in the presence of oxygen, increases the degree of protection of steel and preventing the formation of at its surface carbonate-calcium deposits.

Key words: corrosion of water circulation systems, carbon steel, temperature, flow rate, cathodic inhibitors, and calcium carbonate deposits.

INTRODUCTION

It is known [1-4] that the corrosion rate of heat transfer equipment is influenced by many external factors and, in particular, the temperature and the rate of coolant flow, since these parameters are associated with the oxygen supply (for open water cooling systems), which is the main corrosion agent is in neutral and alkaline media. With increase in temperature for every 30°C the corrosion rate increases, on average, twice the rate of diffusion of oxygen increases and decreases its solutions bridge.

The water flow rate is not less important: low speed lead to the formation of stagnant sites, which are centers of local corrosion; high speed impede the formation of the protective film [5-7].

In addition, the water circulation system develops abnormal processes (scaling and accompanied by their mineral deposits), which are caused mainly by physical and chemical changes on the surface of the solid-liquid phase, which creates conditions for scaling corrosion. Determining factors of abnormal processes are the temperature and movement of the circulation water, as well as its composition and chemical properties [8-11].

OBJECTIVES

Objective - to study the effect of water temperature and flow of motion on the corrosion rate of carbon and carbon steel water system in petrochemical enterprises as without, and in the presence of an inhibitory composition.

The experimental procedure. As a corrosive environment served as a model solution simulating open systems most aggressive circulation water refinery following composition: pH - 7.3, the rigidity of the total - 9,2 mmol/dm³, the rigidity of calcium - 8,5 mmol/dm³, alkalinity - 2,5 mg-ekv/dm³, chlorides - 1153,0 mg/dm³, sulfates - 1019,0 mg/dm3, salinity - 3380,0 mg/dm³ [12, 13].

Potentiodynamic and potentiostatic polarization curves filmed using in potentiostat P-5848 at a scan rate of 0,33 mV/s. Potential values were recalculated relative to the normal hydrogen electrode.

The studies were conducted at temperatures of 5, 20,40,60°C, under static and dynamic conditions with a linear flow rate of $0,6 \div 1,4$ m/s. According to the technical regulations of the temperature of circulation water inlet system usually is 25 °C and at the exit of 47°C. The water flow rate reaches 1,4 m/s. The corrosion rate was determined by gravimetric method as per GOST 9.506-87. Character corrosion damage to steel examined under an optical microscope, the composition of deposits - chemical analysis. The inhibitor composition used " SVOD-BI » with optimal concentration for waters of similar composition - 40 mg/dm³ [14-16]

Bench tests were carried out at the facility, simulating the heat exchanger, the volume of 30 liters at t = $40 \text{ }^{\circ}\text{C}$ on samples made of St3.

Results and its discussion. Test samples St3 model solution recycled water refinery found that the corrosion rate increases linearly with increasing temperature of the solution (Fig. 1, curve 1) and the value it exceeds the permissible limits (up to 0,1 mm/year). By increasing the temperature to 20°C the corrosion rate increases by $0,17 \div 0,28$ mm/year, those average becomes twice. The nature of this dependence is defined as the temperature increases, simultaneous action in opposite directions of two factors: on the one hand, increase the corrosion soon, on the other - reducing the solubility of oxygen, which promotes the formation of oxide barrier films.



Fig. 1. The corrosion rate of the samples of St3 in the model solution circulating water depending on the temperature: 1 - without inhibitor, 2 - supplemented with 40 mg/dm^3 inhibitor

Under static conditions, metal corrosion is limited by the supply of oxygen and corrosive ions to the metal surface, so after 50 hours, the samples were covered with loose sediments. The analysis of their composition showed that the iron - oxide deposits containing Fe₂O₃ -65,7%, CaO/MgO - 24,3%, the rate of formation of deposits (C_o) is 0,16 mm/year. At a constant temperature throughout the experiment (250 hours), the corrosion rate of the steel changes little, often, due to deposits on the surface in a trend towards a reduction.

Research based steel corrosion rate of the speed of circulating water flow have shown that it has an extreme character, with water speeds $0.6 \div 0.8$ m/s reaches the maximum value of the rate of corrosion. At the initial time when loading samples of the largest of its values are observed, for all flow rates studied, whereas with time corrosion is reduced by $20 \div 50\%$. The higher the flow rate, the greater the decrease, which is due, firstly, to form on the steel surface deposits which block the active corrosion centers and, secondly, to increase the oxygen supply rate, which promotes the formation of protective oxide films. Dissolved oxygen in the water flow causes additional electrode OH process to form ions, which lead to increasing the pH of the water in the immediate vicinity of the metal surface and Fe^{2+} ions is oxidized to Fe³ [17]. With constant stirring sol-ditch with flow rate of 1 m/s, the corrosion rate became increased with increasing temperature, two or three times.

Visual examination of the surface of the St3 samples at flow rates of 0,6 m/s 1,0 m / s in 50 hours on the entire surface of the metal formed dense deposits in some areas - iron - oxide. The main component is calcium carbonate deposits, Fe_2O_3 content - 20,7%, CaO/MgO - 70,3%, but under deposits visible ulcerous lesions.





Fig. 2. Corrosion rates of St3 in model solutions at different flow rates of recycled water (40 °C) through: a - 50 hours, b - 250 hours

After 250 hours in a stationary model circulating water solution revealed that the surface of the metal exposed to corrosion spots (Fig. 3), in some places there are pits that are concentrated in small areas, and contributes to the rapid decommissioning of proproduction cycle. When the flow of 0,6 m/s speed through the 250 hours for a total reduction rate corrosion, the depth and area of the ulcer becomes larger (Fig. 3, b). Water flow delivers oxygen to the corroding surfaceboiling and can take it with products of corrosion, which might slow down the accumulation of further corrosion, but plentiful supply of oxygen to the cathode portions activates localized corrosion. However, at a flow rate of 1,0 m/s is observed more uniform dissolution of metal (Fig.3, b), the surface takes the form of "orange" peel as the accumulated deposits sealed and inhibit corrosion processes. Thus, in order to reduce corrosion petrochemical plant equipment, should be encouraged circulating water flow rate 0,4 m/s and above 1,2 m/s.







Fig. 3. The specimen surface after deposition St3 with 250 hours of the model solution in depending on the flow rate v (of recycled water 40°C),: a - 0 m/s; b - 0.6 m/s; c - of 1.0 m/s; d - in the conduct of 40 mg/dm³ of inhibitor at 0.6 m/ s - (× 60)

According to the results of the factor of change of circulating water flow rate equally, and in some cases more, in comparison with the temperature factor that affects the rate of corrosion St3 in open water cycle. Dissolution rates of carbon steel in the circulating water in all the experiments exceeded the permissible value and, consequently, the need arose decrease of its aggressiveness. It should be noted that the regulation and reduction of corrosion losses of an optimal operating

conditions of water circulation systems due to changes in water temperature regime is more complex and energyintensive task than its velocity.

Potential corrosion sate velocity St3 in model solutions equal to 0,24 V, for samples characterized by a high corrosion current. When cathodic polarization current density of steel increased slightly, at the same time while the anode is observed a significant increase in current density, those, steel corrodes with speed, which is limited, mainly the rate of oxygen delivery, which allows the use of cathodic inhibitors or inhibitors of mixed type [18].

Studies in model solution with the introduction of 40 mg/dm³ composition " SVOD-BI ", showed that without stirring rate of corrosion of metal through the 250 hours of the experiment amounted la 0,046 mm/year. On the polarization curves (fig. 4) shows that the administration of a composition reduces the density currents in a wide range of capacities and sate velocity shifts toward more negative potentials, reduction of corrosion processes is due to the formation on the surface of steel with a sparingly-compounds (film).

After gravimetric testing on samples St3 visible protective film of violet, blue and light blue (depending on the thickness of the film), which were loose, easy washable carbonate deposits. On the treated surface became water flow hinders their formation. Peeled sediment samples of products have a clean, shiny surface (Fig. 3d), pits, ulcers were no observed.



Fig. 4. Polarizing cathodic (1,2) and anodic (3,4) curves of St3 in model solution of recycled water solution at 0.6 m/s, $40 \text{ }^{\circ}\text{C} - 1$, 3, and with the introduction of 40 mg/dm³ of inhibitor - 2.4

The experimental data in the recycled water in the presence of the inhibiting composition in the first hours showed the proportional reduction in the corrosion rate of St3 with increasing water flow rate (Fig. 5, a), which is connected by the presence of phosphate in the composition of the inhibitor, which contribute to the growth and to strengthen the oxide film with the participation of oxygen. At a flow rate of circulating water inhibited 1,2 m/s and higher corrosion processes reduction ceased, those reach respective inhibitor concentration and oxygen supplied. After 250 hours of the

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experiment (Fig. 5, b) the corrosion rate with increasingtion flow rate decreased exponentially, due to the presence of educated and loose calcium carbonate deposits. Thus, the introduction of an inhibitory composition " SVOD-BI " depends bridge corrosion rate of heat transfer equipment from St3 from the circulating water flow rate becomes not a major factor. Over time $(250 \div 300 \text{ hours})$, the film is gradually destruction and violated its continuity. For a while there remains passivated steel by supplying oxygen to the pores of the film, but gradually the area has increased, corrosion processes are activated and a system needs a recharge inhibitory composition.

It should be noted that earlier, in [19, 20], we work the concentration of composition 40 mg/dm³ was recommended at a temperature of 40°C, the degree of protection of steel is low and amounts to an average of Z=69%, but the rate of corrosion is within acceptable limits. However, according to the results to provide reliable protection of steel, especially when production stops, when the cease-circus recycled water, is necessary to increase its concentration. Experimentally determined that optionally on average, double the amount of the inhibitor with the level of protection Z reaches 92%.







Fig. 5. Corrosion rate of St3 in model solution of recycled water with the introduction of inhibitor 40 mg/dm^3 , 40° C at different flow velocities v through: a - 50 hours, b - 250 hours

CONCLUSIONS

1. Through the study of the influence of temperature and flow rate of circulating water on the corrosion rate St3 found that increasing temperature leads to a linear increase in corrosion rate, whereas increasing the circulating water flow rate is extreme.

2. The maximum increase in corrosion rate is three to four times necessary when v = 0.6 m/s, while the temperature increases to 20 °C corrosion rate increased by an average factor of two.

3. Additional oxygen supply, and composition changes lead to an increase of localized corrosion. In order to reduce equipment corrosion petrochemical plant, it is necessary circulating water flow rate varied up to 0,4 m/s and above 1,2 m/s.

4. The use of cathodic inhibitors or inhibitors of mixed type can significantly reduce the effect of temperature and flow rate of corrosion on St3, promotes the growth and strengthening of oxy-discharge of the film in the presence of oxygen, increases the degree of protection and prevents the formation on the surface of steel-carbonate-calcium deposits.

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ОСОБЕННОСТИ ВЛИЯНИЕ НЕКОТОРЫХ ФАКТОРОВ НА КОРРОЗИЮ УГЛЕРОДИСТОЙ СТАЛИ В ОБОРОТНОЙ ВОДЕ

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Аннотация. Изучено влияние внешних факторов, температуры и скорости потока, на коррозионные процессы Ст3 в модельных растворах оборотной воды нефтехимического предприятия с высоким солесодержанием и жесткостью для открытых систем без и в присутствии ингибирующей композиции. Выявлено, что увеличение температуры приводит к линейному росту скоростей коррозии, а изменение потока оборотной воды приводит к скорости экстремальному характеру коррозионных процессов; определены оптимальные условия. Рекомендовано использование катодных ингибиторов или ингибиторов смешанного типа, в частности, композиции «СВОД-БИ», которая позволяет существенно снизить влияние температуры и потока на скорость коррозии СтЗ, способствует росту и укреплению оксидной пленки в присутствии кислорода, повышает степень защиты стали и препятствует образованию поверхности ее на карбонатно-кальциевых отложений.

Ключевые слова: коррозия водооборотных систем, углеродистая сталь, температура, скорость потока, катодные ингибиторы, кальциевые и карбонатные отложения.