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CORROSION OF GALVANIZED PIPES IN HOT WATER SYSTEMS

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ABSTRACT

The studies were carried out in order to determine the causes of the formation of a through corrosion defect on the galvanized pipe of the hot water supply system (HWS) Ø42 × 3.5 mm, after operation for two years. The study included visual and optical inspection of pipes, analysis of the chemical composition of metal and corrosion products on the inner surface of the pipe, analysis of the chemical composition of water, as well as a set of electrochemical tests conducted at temperatures of 20 and 60 °C. It was found that the main reason for the formation of the through corrosion defect was the low quality of the zinc coating on the inner surface of the galvanized pipe, the initial state of the coating had a significant roughness, and its thickness varied in a fairly wide range from 4 to 55 μm. Furthermore, during the two years of operation at 55 ° C water temperature in the HWS system, due to passivation, the zinc coating potential becomes more positive than the steel potential, and the zinc coating loses its protective properties by becoming cathodic in relation to steel. In the future, conditions are created for accelerated local anode dissolution of the sections of the galvanized pipe that lacks zinc coating, with the formation of through corrosion defects.

KEY WORDS: *galvanized steel, hot water system, corrosion potential, corrosion rate.*

INTRODUCTION

The operation of domestic water supply systems, hot water supply (HWS) on domestic hot water pipelines in high-rise buildings assembled from galvanized pipes with a service life of not more than 2–4 years is associated with the problem of corrosion development. According to the results of the study of heating systems and HWS, the cause of through defects were inaccuracies in the power supply system, which led to the introduction of industrial frequency pipelines with a current of 0.1 to 18.2 A [1]. In studies of the Gdansk HWS, which worked for no more than four years, showed that there was no zinc coating on the internal surface of the galvanized steel pipeline [2]. The main causes of the corrosion process were high oxygen levels and carbonic acid concentrations, as well as high concentrations of chloride and sulfate ions. Additionally, microbial corrosion is also considered as the reasons for accelerated corrosion of galvanized HWS pipes with small water withdrawals [3]. In general, the scientific publications have little information on the corrosion of galvanized pipes of internal HWS.

The aim of this work was to determine the causes of the formation of a through corrosion defect on a HWS galvanized pipe of one of the hotels in Kyiv, after two years of operation.

MATERIALS AND METHODS

Electric-welded pipes Ø42×3,5 mm with zinc coating applied to the external and internal surface of the pipe by hot dip galvanizing according to [4-5] in the initial state and after operation pipe in the HWS(Fig. 1), which was dismantled during the emergency repair.

Metallographic investigations of micro-sections were carried out on fragments of galvanized pipes in the initial state and after HWS operation. The production of micro-sections included polishing with sandpaper with grit from 80 to 2500, polishing paste with 0.3 microns abrasiveness and etching in Nital.

A visual assessment was carried out by Neofot-21 optical microscope with a × 320 magnification. The chemical composition of the base metal of the pipe was determined by Bird Spectra-1000 optical emission spectrometer. Analysis of corrosion products on the pipe internal surface was evaluated by Camebax SX 50 scanning electron microscope.

<center>*a*   *b*</center>

Fig.1. The galvanized pipe internal surface in the initial state (*a*) and after operation (*b*).

Sampling of water for analysis was carried out according to [6], and chemical analysis of water was carried out in accordance with standards [7]. Molecular oxygen concentrations in water were determined by Cyber Scan PD300 oximeter. The analysis was performed in water coming from the water utility network and after a four-stage water purification system.

Gravimetric studies of the steel corrosion rate were performed on specimens of size 20×6×3 mm, cut from the base metal of a galvanized pipe Ø42×3.5 mm. The zinc coating was removed from the surface by sequential grinding with sandpaper with a grain size of 80 to 2000. Samples were washed in running and distilled water, dried, wiped with ethanol and left for 24 hours in a desiccator, then weighed on analytical balance to the nearest 0,00005 g. The tests were carried out on the water samples described above. The test duration was 12 days. After testing, the samples were cleaned from corrosion products, washed in running and distilled water, dried, wiped with ethanol and left for 24 hours in a desiccator, and then weighed on analytical balance to the nearest 0,00005 g. According to the measurement results, the mass (K_m) and depth (K_n) corrosion rates were calculated by the formulas:

$$K_m = \frac{\Delta m}{S \cdot \tau}, \ (\frac{g}{m^2 \cdot year}) \text{ and } K_n = 8,76 \cdot \frac{K_m}{\rho}, (mm \ year^{-1}) \tag{1}$$

where Δm is the weight loss of the sample after testing, g; S - sample area, m^2; τ - duration of tests, hours; ρ - metal density, $g \ cm^{-3}$; 8.76 - conversion coefficient.

UISK-101 apparatus performed measurement of corrosion rate by the polarization resistance method. For measurements, a flat coplanar two-electrode sensor with a single electrode size of 30×7×3 mm, which was made of the base metal of the corroded pipe Ø42×3.5 mm without zinc coating, was used. In the second phase, the corrosion rates of steel and zinc coating in water after water treatment were determined at temperatures of 20 °C and 60 °C. The already developed steel two-electrode sensor, as well as a flat two-electrode sensor with a zinc coating on both sides, the size of a single electrode 30×7×3 mm, were used. For study the electrochemical behavior of zinc when temperature changing of the corrosive environment, an additional measurement of the corrosion rate was carried out immediately after the temperature decreased from 60 °C to 20 °C on a zinc-coated sensor. The uncoated zinc sensor electrodes surfaces were chemically resistant lacquer coated. The corrosion rate was calculated by the formula [8-9]:

$$i_k = \frac{K}{R_p} = \frac{K \cdot \Delta I}{\Delta E}, \ (mm \ year^{-1}) \tag{2}$$

where K – estimated sensor coefficient (for steel–167, for zinc–214), Ω mm year^{-1}; ΔI – current arising between the electrodes, A; ΔE – potential difference, V; R_p – polarization resistance, Ω.

Potential measurements were performed on the external and internal surfaces of galvanized pipes Ø42 mm in the initial state and after operation (after removal of corrosionproducts). The tests were performed in water samples after water purification. The surface potentials relative to the chlorine-silver reference electrode were measured below the drop using a Lugin capillary. The duration of the potential measurement at one surface point was 1 hour.

The measurement of current-voltage characteristics carried by PI-50.1 potentiostat and the PR-8 programmer using a clamping electrochemical cell according to a three-electrode measurement scheme.Corrosion polarization test was performed in water after water treatment at temperatures of 20 °C and 60 °C at a scan rate of 1 mVs[-1]. The test sample was kept as working electrodeand the working electrode

exposed area was 10^{-5} m². The working electrode was kept in solution for 30 min, until the stationary potential was established, followed by polarization. All tests were performed under free air aeration.

RESULTS AND DISCUSSION

According to the visual inspection of galvanized pipes Ø42×3.5 mm (initial state and after hot water supply system operation) it is established that zinc coating on the outer surface of the pipes, was shiny, smooth and uniform without visible corrosion marks in the both pipes. The initial thickness of the zinc coating on the pipe outer surface ranged from 40 to 57 μm (Fig. 2 *a*). On the pipe inner surface the thickness of the zinc coating was uneven due to the considerable roughness (Fig. 1*a*) and ranged from 4 to 55 μm (Fig. 2 *b*), which was confirmed by the results of the micro-grinding analysis. The pipe inner surface after HWS operation was covered with loose brown color corrosion products (Fig. 1*b*), after the removal of which the absence of zinc coating was observed on the pipe separate sections, which was confirmed by the microscopic analysis results (Fig. 2*c*).

| *a* | *b* | *c* |
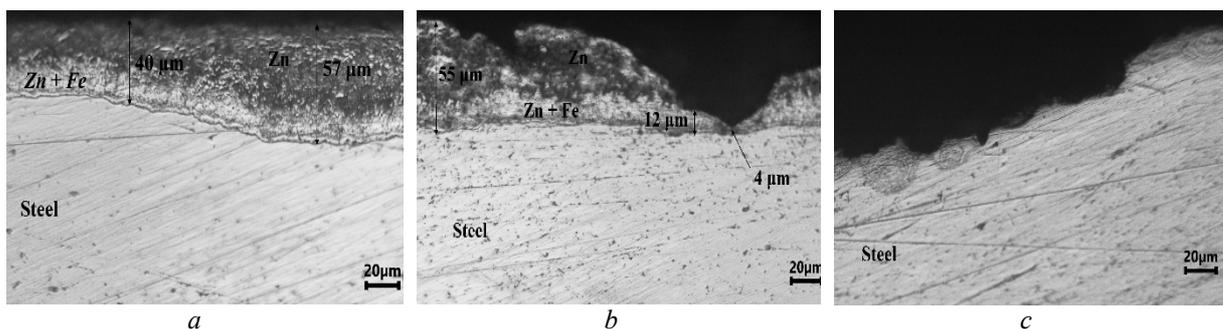
Fig.2. Cross-section of zinc coating onthe pipe outer wall (*a*) and on the pipe inner wall (*b*) in the initial state, and the pipe inner wall after HWS operation (*c*).

According to the results of the elemental composition analysisof the base metal (Table 3.1), it was found that the pipe material corresponds to the low carbon steel 08kp [10]. According to the results of the analysis of the corrosion products (Table. 3.1), the main part of 97,955 wt. % is iron, zinc and oxygen, so it can be assumed that the corrosion products on the pipe inner surface are predominantly composed of iron oxides and hydroxides $Fe(OH)_2$, $FeOOH$, FeO, Fe_3O_4, as well as zinc hydroxide $Zn(OH)_2$.

Table 3.1. Chemical composition of base metal (A) and corrosion products (B), %

		C	Si	Mn	S	P	Cr	Ni	Ti	Al	Ca	Fe	Zn	Mg	O
A	In initial state	0.1	0.009	0.51	0.008	0.015	0.03	0.04	<0.002	-	-	-	-	-	-
	AfterHWS	0.157	0.006	0.33	0.022	0.009	0.05	0.04	<0.002	-	-	-	-	-	-
B		-	0.719	0.059	0.139	-	-	-	-	0.375	0.153	33.86	19.9	0.6	44.195

It can be assumed that the formation and accumulation of corrosion products on the pipe inner surface occurred by the following reactions:

$$2Zn + O_2 + 2H_2O \rightarrow 2Zn(OH)_2 \tag{3}$$
$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2 \tag{4}$$
$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \tag{5}$$
$$Fe(OH)_2 \leftrightarrow FeO + H_2O \tag{6}$$
$$Fe(OH)_3 \leftrightarrow FeOOH + H_2O \tag{7}$$
$$2FeOOH \leftrightarrow Fe_2O_3 + H_2O \tag{8}$$
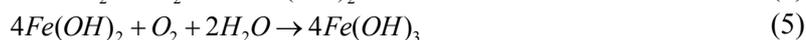
According to the results of the chemical analysis of water quality (Table 3.2), it is established that by most indicators water samples meet the standards [7]. The content of dissolved oxygen, free carbon dioxide and the equilibrium saturation index of calcium carbonate are sufficient for an intensive oxygen corrosion.

Table 3.2. Chemical analysis of water quality

Test water	pH	Totalhardness, mg-eq l^{-1}	Ca^{2+}, mgl^{-1}	Mg^{2+}, mgl^{-1}	Cl^-, mgl^{-1}	O_2, mgl^{-1}	HCO_3^-, mgl^{-1}	$Fe^{2+,3+}$, mgl^{-1}	CO_{2free}, mgl^{-1}	Equilibrium saturation index of calcium carbonate
1	7.4	3.5	50.1	12.16	28,4	7.72	158.6	0,20	10.56	-0.5
2	7.35	3.6	52.1	12.16	28.4	6.45	158.6	0.18	10.12	-0.25
norm [7]	6.9-9.0	7.0	-	-	350	-	-	0.3	< 5	from 0.1 to 0

According to the results of corrosion rate measuring (Table 3.3) by gravimetric (K_m) and polarization resistance methods (K_n), it is established that the steel corrosion rate in water before and after the water treatment system is almost indistinguishable. Given this, further studies were conducted only in water after water treatment.

Table 3.3. The corrosion rate of steel

	K_m, g m^{-2} $year^{-1}$	K_n, mm $year^{-1}$	i_k, mm $year^{-1}$
1	0.073	0.084	0.095
2	0.075	0.086	0.097

According to the results of measuring the corrosion rate of steel (Fig. 3 *a*) and zinc coating (Fig. 3 *b*), it is found that increasing the water temperature from 20 °C to 60 °C, increases the steel corrosion rate by about 2 times from 0.09 mm $year^{-1}$ to 0.148 mm $year^{-1}$ after 3 hours of measurement. On the zinc coating, with increasing water temperature from 20 °C to 60 °C, the corrosion rate increases from 0.068 mm $year^{-1}$ to 0.099 mm $year^{-1}$. Repeated measurement of the corrosion rate of zinc at 20 °C after 3 hours at 60 °C showed a further decrease in the zinc corrosion rate to 0.048 mm $year^{-1}$, which can be explained by the formation of passive zinc hydroxide film. The latter is a negative factor that can lead to both partial and complete passivation of the zinc coating and the loss of its protective properties towards to steel.

In Fig. 4 shows the results of measuring the corrosion potentials on the outer and inner surfaces and base metal of the galvanized pipe in the initial state, as well as on the zinc coating and base metal (corrosion defect) of the pipe inner surface after operation. As can be seen in Fig.4, the corrosion potential of the pipe outer surface -0.987 V (Fig. 4 *a*) and the inner ones -0.976 V (Fig. 4 *b*), i.e. they correspond to the standard potential of zinc, and the potential of the base metal -0.576 V (Fig. 4 *c*) corresponds to the corrosion potential of steel. On the pipe inner surface after the operation and removal of loose corrosion products, the corrosion potential -0.657 V (Fig. 4 *d*), which is more negative than steel, but much lower than the supply zinc potential, which can be explained by the significant passivation of the zinc coating. That is, it is confirmed the assumption of the loss of the protective properties of the zinc coating.

As can be seen in Fig. 5, according to the obtained polarization curves with increasing water temperature from 20°C to 60°C, the zinc coating stationary potential shifts to the anode region from -1.1 V to -0.87 V, with the speed of cathodic processes of reduction from oxygen water and hydrogen, are projected to accelerate approximately 10 times. On the anode curve at 20°C, the zinc passivation region isobserved in the anode polarization region from -1.0 V to -0.9 V, with the subsequent transition to the active dissolution region. At a temperature of 60ºC, the transition of zinc to the passive state at anode polarization is not observed.
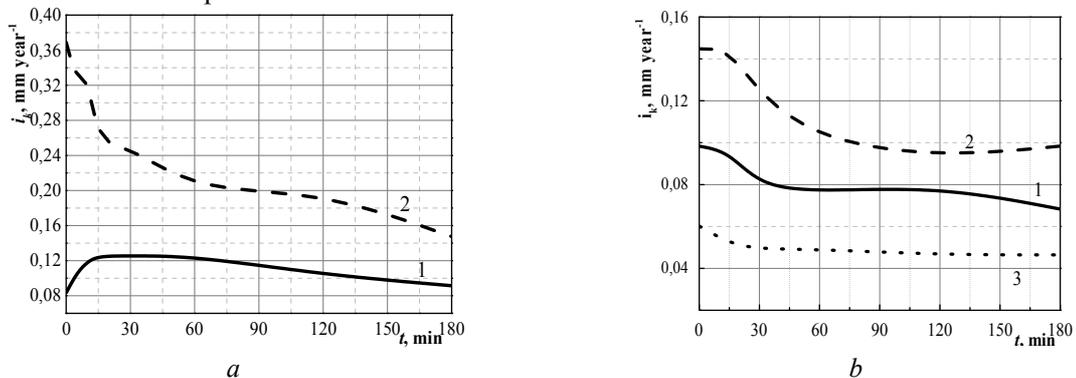
Fig.3.Corrosion rate of steel (a) and on zinc (b) obtained with polarization resistance methods in water after water treatment at 20 °C (1), 60 °C (2) and at 20 °C after holding at 60 °C (3).
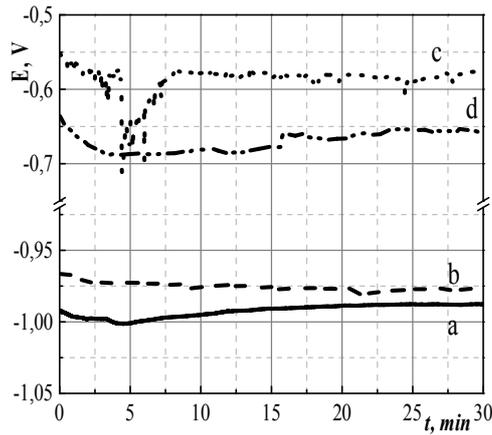
Fig.4. Corrosion potential of galvanized pipe on external (*a*) and inner (*b*) surfaces, base metal (*c*) in the initial state and inner surface after operation (*d*).
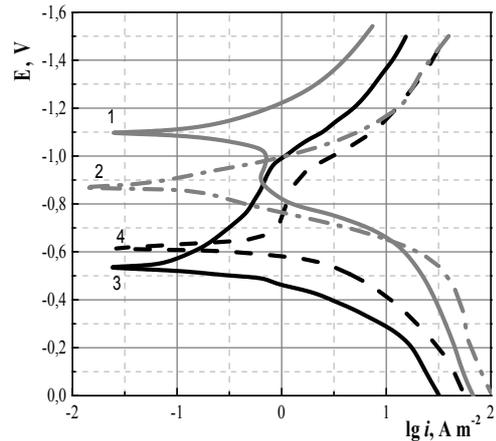
Fig.5. Current-voltage polarization curves ofzinc coating (1, 2) and steel base metal (3, 4) of galvanized pipe at 20 ºC (3), 60 ºC (2, 4).

Increasing temperature promotes the shift of the stationary potential on the pipe base metal into the cathode region from -0.54 V at 20 ºC to -0.62 V at 60 ºC. In addition, as the temperature increases, acceleration of both cathodic (oxygen and hydrogen reduction) and anode processes (steel dissolution) is predicted.

Summarizing the above results, it can be assumed that the formation of a through-corrosion defect on the galvanized pipe of the hotel's HWS occurred through a series of successive steps. At the water operating temperature in the HWS 55 ÷ 60 ºC and the presence of sufficient oxygen and carbonic acid in the water, an active anodic dissolution of the zinc coating and cathodic oxygen reduction by reaction occurs (4). Considering the high rates of anode dissolution of zinc and its considerable unevenness in thickness, because of corrosion, uncover steel pipe sections without zinc coating are formed, which also begin to actively dissolve with the formation of iron ions. Over time, due to the corrosion of the zinc coating, and the deposition of steel corrosion products on its surface, it is passivated, and the corrosion potential of the zinc coating gradually shifting to the cathode side, approaching the corrosion potential of steel and at some point takes on a more positive value than the potential of steel. Subsequently, the zinc coating becomes cathodic in relation to the pipe base metal (steel), i.e., completely loses its protective properties. In the free corrosion conditions of the galvanized pipe, the corrosion rate will be determined only by the ratio of the areas of the anode and cathode sections, and after passivation, the internal zinc-coated surface acts as a cathode, where the oxygen reduction reaction flows, and the exposed sections of the pipe inner surface are exposed as anode. For example, if the cathode sections area is a hundred times more than the anode sections area, then:

$$i_k^c = i_k^a = \frac{I^c}{S_c} = \frac{I^a}{S_a} \tag{9}$$

$$\frac{I^c}{I^a} = \frac{100 \cdot S_a}{1 \cdot S_c} = 100 \; times \tag{10}$$

$$I^c = 100 \cdot I^a \tag{11}$$

where i_k^c, i_k^a – the cathode and anode processes rates, Acm^{-1}; I^c, I^a –cathode and anode currents, A; S_c, S_a –the cathode and anode sections area, cm^2.

That is, the anodic dissolution rate of metal (corrosion of steel) will be one hundred times higher than the speed of the cathodic process (oxygen reduction), which ultimately leads to the formation of local through defects.

CONCLUSIONS

According to the results of the study from this research work, the following is established:

- Chemical analysis of water quality by most indicators meets current standards, but the content of dissolved oxygen, free carbon dioxide and the equilibrium saturation index of calcium carbonate is sufficient to take place intensive corrosion with oxygen depolarization;

- Zinc coating on the galvanized pipe internal surface in the initial state has a considerable roughness, and its thickness varies in a fairly wide range from 4μm to 55 μm, which indicates its low quality.

- On corroded pipes after two years of operation in the HWS, the entire internal surface was covered with brown corrosion products, the chemical analysis of which showed the presence of iron oxides and hydroxides as well as zinc hydroxide in them.

- Increasing the water temperature from 20 °C to 60 °C, leads to the rapid dissolution of areas where the zinc coating has the lowest thickness. Over time, the corrosion rate decreases due to the passivation of the zinc coating, with the potential becoming more positive than the steel potential, and the zinc coating loses its protective properties becoming cathodic with respect to steel. In the future, conditions are created for accelerated local anode dissolution of the galvanized pipe sections where zinc coating is missing, with the formation of through corrosion defects.

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