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COMPARATIVE ASSESSMENT OF CORROSION BEHAVIOUR OF MILD STEELS 3, 20 AND 08KP IN TAP WATER

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Abstract. Comparative assessment of corrosion stability of mild steels 3, 20 and 08KP in tap water was conducted. Similar corrosion behavior of these steels was shown by weight loss, linear polarization resistance and polarization curves techniques both for pretreated and corroded surfaces. The discrepancy of the results obtained with the LPR and weight loss techniques was found out and its possible reasons were discussed.

Keywords: corrosion, mild steel, water supply, corrosion monitoring, polarization resistance.

1. Introduction

Fail-safe operation of district heating (with water used for heat distribution) and drinking water supply systems is of tremendous importance for sustainability of modern megapolises. Current national standards of the former SU countries [1, 2] define materials to construct water piping networks. Predominant use of steel welded pipes [3] in construction and maintenance of district heating and water supply systems is conditioned by numerous factors: ease of installation, manufacturability of parts, well-established pipe-connecting procedure, large offer of dimension types, and cost. Most commonly used mild steels are: Grade 3 Steel [4], Grade 20 Steel, and Grade 08KP Steel [5]. Those steels tend to corrode in water media with oxygen depolarization. Inner pipe corrosion causes 25 % of water supply systems failures [6], leads to water quality worsening, leakages, water loss, territory flooding. This is why steel corrosion is both an ecological and an economical problem.

The solution of corrosion problems must include permanent and accurate corrosion monitoring. There are different approaches to corrosion monitoring. Application of defectoscopes is one of them [7]. These instruments are useful for well-timed detection of nascent and already existing cracks and breakdowns. However, for continuous control of water corrosivity methods based on instantaneous corrosion rate measurements, the linear polarization resistance technique (LPR) in particular, appeared most suitable [8]. The advantages of LPR technique are clear: the possibility of its automating [9], non-destructive on-site measurements, relatively simple equipment, and the speed of obtaining results (less than one minute) [10]. At the same time LPR method employs probe electrodes to determine corrosion rates and it is often the case that the electrodes and water piping networks under electrochemical corrosion monitoring are made of different grades of steel. It is assumed that the results obtained with probe electrodes are valid for other elements of the piping network. Obviously, such an assumption is justified if corrosion processes on different grades of mild steel are identical. It is shown [11] indeed, that a constant of proportionality between polarization resistance and corrosion rate in acidic media is not influenced by steel grade for steels 08, 10, 15, 20, 25, 35, 45, and Steel 3. An average value of constant B was 30 mV in 1N H_2SO_4 and 22.3 mV in 6N H_2SO_4 for all studied steel grades.

It is known that steel composition affects its corrosion behaviour. For example, while mild steels 20 and 17G1S have a low amount of alloying components, they have been shown to demonstrate a different propensity towards local corrosion [12]. Therefore, in order to obtain the representative value of corrosion rate of a water piping network by means of the LPR method a comparative evaluation of corrosion behaviour of different grades of mild steel is necessary.

2. Experimental

Weight-loss, LPR and polarization curves methods were used in corrosion measurements.

Table 1

Steel chemical composition

Steel grade	C, %·100	Mn, %·100	Si, %·100	S, %·1000	P, %·1000	Cr, %·100	Ni, %·100	Cu, %·100
3	16	56	6,9	39	22	3.9	1.6	3.2
20	20	39	20	14	16	6	9	16
08KP	7	35	1	27	23	2	2	3

Table 2

Tap water parameters

Parameter		Measurement units	Value
Total hardness	TH	mg-eqv/dm^3	3.9–4.2
Total alkalinity	TA	mg-eqv/dm^3	3.9–4.1
Calcium	Ca^{2+}	mg-eqv/dm^3	3.0–3.1
Magnesium	Mg^{2+}	mg-eqv/dm^3	0.9–1.1
Chloride	Cl^-	mg/dm^3	4–6
Sulfate	SO_4^{2-}	mg/dm^3	30–35
Hydrocarbonate	HCO_3^-	mg-eqv/dm^3	3.2–3.5
Total dissolved salts	TDS	mg/dm^3	240–260
Hydrogen index	pH		7.4

Cylinder-shaped samples made of mild steel 3 and steel 20 had a length of 30 mm and a diameter of 6 mm. The inner screw-thread was made on one side of the cylinder to input current. 20x30 mm steel plates were cut from 1.5 mm thick sheet of steel 08KP. The elemental composition of the steel grades used in the present study is given in Table 1. The samples before measurements were mechanically grinded with SiC abrasive paper of P180 grit, rinsed with distilled water, cleaned with filter paper and dried in air.

Tap water from Solomyanskiy district, Kyiv, was used as a medium in corrosion tests. The water has a composition that is typical of inhabited localities in the Dnipro river basin; its main parameters are listed in Table 2.

Weight-loss measurements were conducted according to the standards [13]. The samples were weighted with the accuracy up to 0.00005 g prior to the experiments. After exposure to tap water loose corrosion products formed on the sample surface were removed with a soft rubber. Adherent solid corrosion products were removed using 20 min exposure of the samples to 100 g/dm^3 H_2SO_4 etching solution that contained 5 g/dm^3 of thiourea [14] as a corrosion inhibitor. The length of exposure to tap water – 1, 2, 3 weeks, 4 samples each time period.

LPR measurements were performed on a PIK-1 instrument that operates in a galvanostatic mode. PIK-1 is an advanced analogue of the LPR instrument P5126, which is imposed by standards [15]. A two-electrode LPR probe with electrodes made of the investigated steel grades was connected to PIK-1. The initial differences of potentials and ohmic losses in solution were compensated automatically during measurement. In order to decrease influence of the polarization capacity on the results the instrument applies the two-step corrosion measurement scheme [16]. Experiments were run on electrodes used further in the weight-loss measurements. 6 probes were installed in the cell of 1200 cm^3 volume. The length of the experiment was 21 days.

Polarization curves were measured on a freshly grinded surface using a PI-50-1.1 potentiostat with computer data logging at 291 ± 2 K without stirring. A traditional three-electrode cell was used in electrochemical measurements. Working electrode was made of the investigated steel (with working area of 0.5 cm^2), a silver chloride electrode (E = 0.222 V/NHE) was used as a reference electrode and an 8 cm^2 platinum plate as an auxiliary one. The cell volume was 150 cm^3. A potential sweep rate was 0.5 mV/s; the scanning range was ± 300 mV starting from the free corrosion potential. Current–potential curves were recorded twice on each electrode to ensure results convergence. The water had the same composition as in the weight loss experiments (Table 2).

3. Results and Discussion

Polarization curves are shown in Fig. 1.

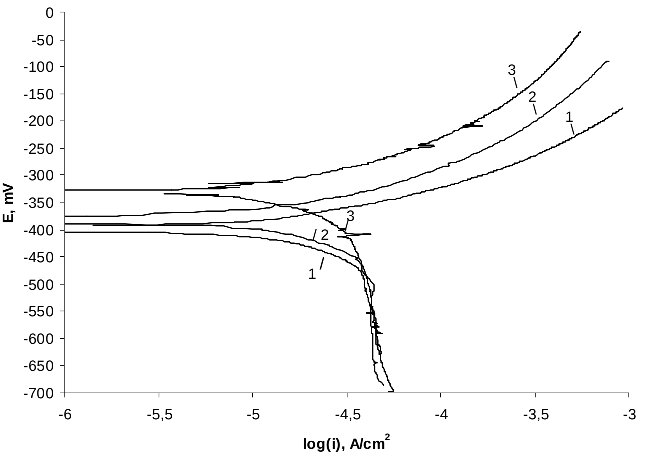

Fig. 1. Polarization curves obtained on freshly grinded surfaces in static conditions in tap water for different types of steel: steel 3 (1); steel 20 (2) and steel 08KP (3)

Kinetic parameters of the polarization curves are listed in Table 3.

Table 3

Kinetic parameters of the polarization curves

Parameter	Units	Steel 3	Steel 20	08KP
E_c	mV	-403	-398	-328
I_c	$(4.3–4.4)\cdot10^{-5}$, A/cm^2		0.475, mm/year	
b_a	mV	60.6	62.5	61.9
b_c	mV	∞	∞	∞
B	mV	26.3	27.1	26.9

An anodic branch of the curves shows a typical exponential dependence of iron ionization current on the applied potential. An experimental Tafel slope b_a was determined to be of 60–63 mV. The proportionality constant B, which relates the polarization resistance R_p to the corrosion current can be calculated using the formula $B = b_a/2.3$ for the reaction on limiting current (when $b_c = \infty$). The calculated values of B for the steel grades studied fall within the range of 26.3–27.1 mV.

A limiting current plateau at cathode potentials in the range from -450 to -650 mV/NHE is observed on cathode branches for all the samples, which corresponds to dioxygen reduction. The values of limiting current are almost equal for the steel grades studied (Table 3).

Stationary potentials of the steels lie in the range of (-400)–(-330) mV/NHE and are easily reproducible. The time required for stationary potential to set in is 15–20 min after immersion.

Values of corrosion rate obtained from the results of the weight loss measurements are shown in Fig. 2.

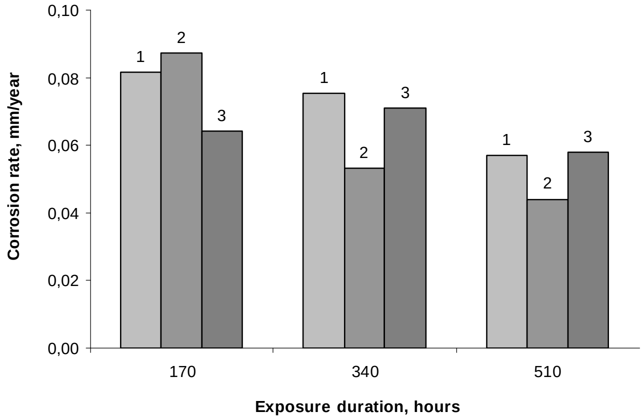

Fig. 2. Weight loss corrosion rate *vs*. time for steel grades: steel 3 (1); steel 20 (2) and steel 08KP (3)

As can be seen from the diagram corrosion rates of the investigated steels are close. Corrosion rate remains highest during the first week reaching the level of 0.09 mm/year. With time corrosion rate tends to decrease to the values of 0.06–0.04 mm/year for all steels.

Fig. 3 shows plots of the time dependence of polarization resistance.

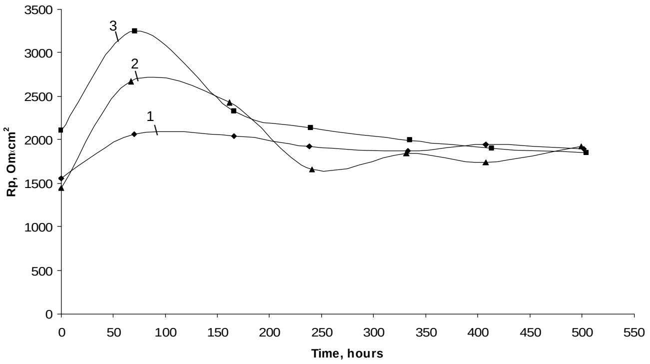

Fig. 3. The time dependence of polarization resistance in static conditions in tap water for different types of steel: steel 3 (1); steel 20 (2) and steel 08KP (3)

The plots for different grades of steel exhibit similar behavior, polarization resistance values are in agreement within the experimental error. An increase of polarization resistance is observed during the first 100 h of the experiment. After 100 h R_p decreases and eventually its value stabilizes at 1500–2000 $\Omega\cdot cm^2$ for all steel types.

Kinetic parameters obtained from the polarization curves are in agreement with the literature data for steel and iron. The value of limiting current of dioxygen reduction by the reaction:

$$O_2 + 2H_2O + 4e^- = 4OH^- \qquad (1)$$

corresponds to the value calculated using the equation of limiting diffusion current in the case of the diffusion layer thickness of 0.041 cm. Such thickness agrees with the data for dioxygen diffusion in static experimental conditions (10^{-1}–10^{-4} cm) [17].

Anodic polarization slopes for steels 3, 20 and 08KP are very close, which indicates similarity of the anodic processes on surfaces of these steels. The slopes correspond to oxidation of metallic iron to Fe^{2+}:

$$Fe = Fe^{2+} + 2e^- \qquad (2)$$

Comparison of kinetics parameters (Table 3) obtained from polarization curves shows similar electrochemical behaviour of freshly grinded surfaces of steels 3, 20 and 08KP. Thus, a slight difference in chemical composition of these grades appeared to be insignificant with respect to their electrochemical behaviour in the experimental conditions of polarization curves measurements.

The analysis of the weight loss data demonstrates that the corrosion rate for all the steels studied decreases with time reaching the level of 0.06–0.04 mm/year. Similar values are reported for those steels by V. Parshutin and co-authors [18], who investigated steel corrosion in water of different composition. Also, the results obtained by the laboratory of water heating systems of MOSENERGO gives the value of 0.04–0.067 mm/year for general corrosion of steel 20 in tap water [19].

Considerable reduction of the corrosion rate after 3 weeks exposure to tap water in static conditions, if compared to the polarization data, is caused by the formation of protective layers of corrosion products and media components on the electrode surface during the exposure. The layers consist mainly of iron oxides and hydroxides with calcium carbonate inclusions [20]. In polarization measurements the freshly grinded electrode surface is free of corrosion products and dioxygen can reduce on the whole area. When steel corrodes in neutral water media corrosion products are accumulated on the surface due to their low solubility and absence of the water flow, thus preventing further corrosion by blocking the surface from dioxygen [21]. An active surface area after 3 weeks of exposure is reduced by 90% based on the ratio of the values of dioxygen reduction current on freshly grinded and corroded surfaces.

The dependence of polarization resistance on time is similar for all the steel grades. Polarization resistance reaches a maximum value during the first 100 h and subsequently decreases down to the value near 2000 $\Omega\cdot cm^2$. These observations also confirm a similarity of corrosion processes with time for steels 3, 20 and 08KP.

Under industrial conditions a corrosion rate value is more convenient than R_p. Polarization resistance can be recalculated to corrosion rate using the conventional constant B = 26 mV [22]. B values of 26.3–27.1 mV that were obtained experimentally in the present work are close to the common value. The plots showing the time dependence of the corrosion rate obtained from the polarization resistance data are shown in Fig. 4. The weight loss results are also presented.

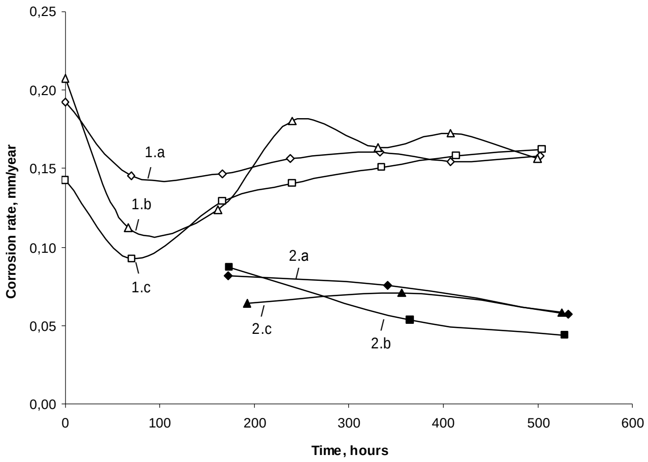

Fig. 4. Time dependences of the corrosion rate measured by LPR (1) and weight loss (2) methods in static conditions in tap water for different steel grades: steel 3 (a); steel 20 (b) and steel 08KP (c)

Comparison of corrosion rates determined by LPR and weight loss techniques revealed that after 170 h of exposure the corrosion rate decreases with time in the weight-loss measurements while in the LPR measurements it increases. Also, a considerable discrepancy (by 2–3 times) between the weight loss and LPR results is observed. As there is no doubt in the weight loss results an explanation is to be searched in the LPR technique.

One of the possible reasons of the observed discrepancy may be the influence of a layer of accumulated iron corrosion products that possesses high electrochemical activity according to [23]. Iron oxohydroxides (FeOOH in α, b, g modifications) can be reduced when polarization is applied to one of the electrodes in the course of LPR measurements. Apparently, their good adhesion to the electrode, a growing amount on the surface and high electrochemical activity set a measured R_p value lower due to the fact that more than one electrochemical process run on the electrode surface during external polarization.

In such a way the rise of R_p during the first 100 h can be a result of formation of a layer of corrosion products that gradually covers the surface. The uncovered surface shrinkage is proportional to the R_p growth; however, the amount of electrochemically active rust is still low. After 100 h the layer that blocks the surface from further dioxygen access, covers the electrode surface almost in full. In these conditions dioxygen transport to the surface is limited causing a decrease in corrosion rate. Nevertheless, R_p values stay low since the external current is consumed to reduce the rust. This leads to a discrepancy between the results obtained with weight loss and LPR methods [23].

Application of different methods to determine corrosion rate of mild steel in tap water showed that electrochemical and corrosion behavior of steel grades 3, 20, and 08KP is similar. These findings make it possible to extend the results obtained for one grade to other grades of low-carbon steel. The most reliable data on corrosion rates is obtained by using the weight loss technique, which is in agreement with the previous observations [23]. LPR measurements do not give true values of corrosion rate as a result of the presence of the electrochemically active rust layer on the metal surface. In order to account for parallel reactions in the course of cathode polarization of the electrode further investigations are required.

4. Conclusions

Corrosion rates of mild steels 3, 20 and 08KP in tap water are close and amount to 0.06–0.09 mm/year (weight loss measurements).

Almost identical electrochemical behaviour of these steels established by weight loss, LPR and polarization curves methods makes it possible to use probe electrodes made of one grade of steel in monitoring of corrosivity of the system made of other steel grades.

A discrepancy in corrosion rate values observed in the LPR and weight loss measurements is caused by electrochemical activity of rust layers on the electrode surface.

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ПОРІВНЯЛЬНА ХАРАКТЕРИСТИКА КОРОЗІЙНОЇ ПОВЕДІНКИ МАЛОВУГЛЕЦЕВИХ СТАЛЕЙ 3, 20 ТА 08КП У ВОДОГІННІЙ ВОДІ

Анотація. *Проведена порівняльна оцінка корозійної стійкості маловуглецевих сталей 3, 20 і 08КП у водогінній воді. Методами масометрії, потенціодинамічних поляризаційних кривих і поляризаційного опору показана подібність корозійної поведінки цих сталей як на свіжезачищеній поверхні, так і після трьох тижнів експозиції. Встановлено розходження результатів вимірювання швидкості корозії методами поляризаційного опору і масометрії та наведено можливі його причини.*

Ключові слова*: корозія, маловуглецева сталь, водопостачання, корозійний моніторинг, поляризаційний опір.*