SPECIFIC CORROSION BEHAVIOUR OF 316L STAINLESS STEEL IN MINERAL WATER

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The comparative assessment of sensitivity to corrosion of the pipe and its welds of 316L stainless steel in the mineral water is made under different electrochemical conditions. The study shows that this steel demonstrates unusual electrochemical behaviour and the typical passive region on the anodic polarisation curve is practically absent. Thus, the steel is electrochemically active in the given environment that provokes its sensitivity to corrosion. It has been found that the preliminary exposure of the specimens to demineralized water saturated with oxygen leads to the appearance of the passive region (plateau) on the anodic polarization curve of steel in mineral water. The length of this plateau increases significantly with increasing exposure time and also with additional applying of the anodic polarization current. The similar trends are observed also for the welded joints of 316L steel. The preliminary treatments of the internal pipeline surface before use are proposed and discussed.

Keywords: *stainless steel, pipeline, mineral water, corrosion current, passivity, oxygen concentration.*

It is well-known that the 316L stainless steel has a high resistance to corrosion in the liquid aggressive environments of different composition that defines its applicability in many fields, such as oil/gas production industry, chemical industry, mechanical engineering, medicine, agriculture sector [1–5], etc.

However, there are some exceptional cases where this steel demonstrates non-standard behaviour, in particular, under its interaction with mineral waters. The corrosion activity of mineral waters arises due to their specific physical properties and chemical composition as well, because their transportation and distribution from different natural sources can sometimes cause the unexpected engineering problems related with the reliability of pipelines under operation [6–9].

The presented study considers the situation with the pipeline for supplying the mineral water to the swimming pools and it can serve as a sample of the above-mentioned problem. This pipeline of a length more than 10 km of the 316L stainless steel is designed, which is very useable and verified for such purposes. However, after one year of operation, the given pipeline system has demonstrated a significant sensitivity to general corrosion and especially to intensive localised corrosion at the welded joints (Fig. 1). The number of such damages has increased in time and the problem of further exploitation of this equipment arises due to the potential possibility of cracks development [10].

With the aim to clarify this situation the proposed study deals with the comparative assessment of the sensitivity to corrosion of the pipe and its welds the 316L stainless steel in the mineral water, which is made for different electrochemical conditions. Here some possible solutions for preventing the corrosion damaging of pipelines for mineral water transportation and improving their reliability in-service are proposed and discussed too.

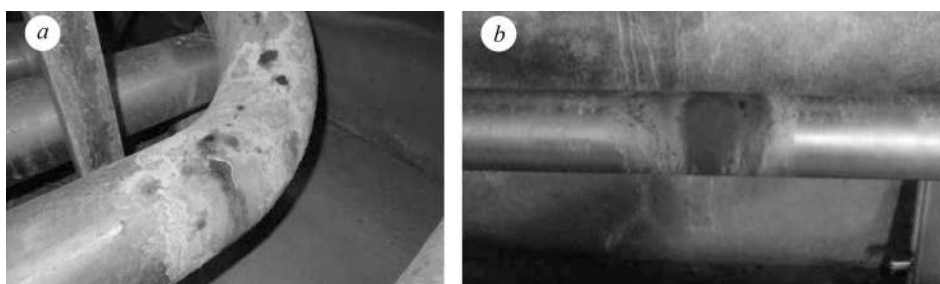*Corresponding author:* J. CAPELLE, e-mail: julien.capelle@enim.univ-lorraine.fr

Fig. 1. Corroded elements of a pipeline for transportation of mineral water:
a – general corrosion of the external surface; *b* – localised corrosion at the welded joint.

Experimental procedure. The pipes and welds of the 316L austenitic stainless steel were the object of study. The chemical composition of the steel is given in Table 1. The specimens were cut from the in-service pipes used approximately for 3 years (Fig. 2). Before testing the specimens were polished and degreased.

The electrochemical tests were conducted in the mineral water (see Table 2) and in the demineralized water at ambient temperature.
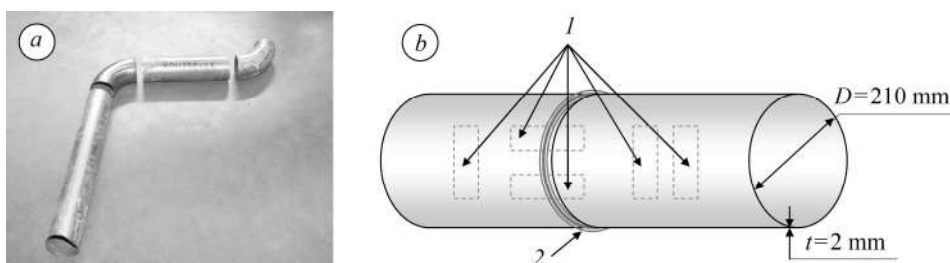

Fig. 2. A pipe with a weld (*a*) and scheme of specimens cutting (*b*): *1* – cutting of specimens; *2* – weld.

Table 1. Chemical compositions of the welded 316L stainless steel (wt.%)

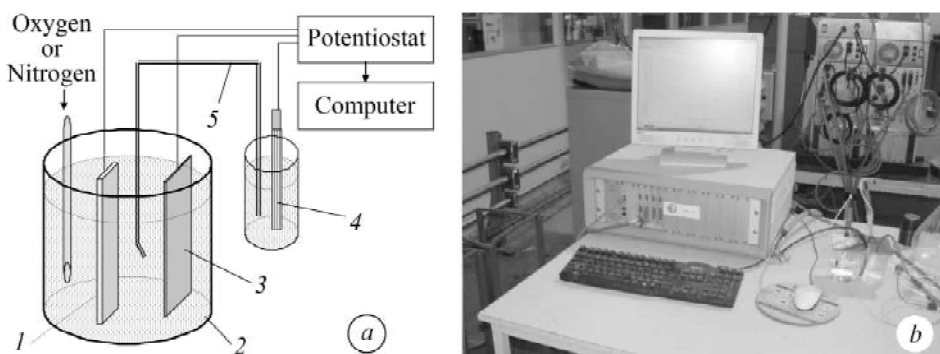| C	Mn	Si	Cr	Ni	Mo	S	P	Cu	Co	Fe
Base metal										
0.019	0.93	0.55	17.4	11.2	2.1	<0.003	0.029	0.28	0.16	Bal.
Weld										
0.027	1.0	0.46	17.0	10.8	2.2	0.004	0.035	0.31	0.13	Bal.

Fig. 3. A schematic view of the electrochemical cell (*a*: *1* – specimen (working electrode); *2* – corrosion cell; *3* – auxiliary (counter) electrode; *4* – reference calomel electrode; *5* – salt bridge and *b*: general view of the testing equipment).

The electrochemical studies were realized with the application of the standard three-electrode electrochemical cell (Fig. 3) with the use of the potentiostat VMP [11].

The potentiodynamic polarization curves for the 316L steel (base metal) and its welds (weld metal) were obtained within the range of potential from –500 mV to +2000 mV. Here the potential scan rate was $dE/d\tau = 50$ mV·s^{-1} for all conducted tests.

The oxygen concentration C_{O_2} in the environment was controlled and the assigned value of this parameter was achieved by bubbling the solution by oxygen or nitrogen.

Table 2. Properties and chemical composition of the mineral water

Mineralization		Iron	<5 µg FeL^{-1}
Conductivity at 25°C	2390 µSm^{-1}	Manganese	5 µg MgL^{-1}
pH	7.40	Oligo-elements – Mineral micropollutants	
Dry sediment at 180°C	1428 µgL^{-1}	Aluminium	<1 µg AlL^{-1}
Dry sediment at 260°C	1424 µgL^{-1}	Copper	<0.01 Cu mgL^{-1}
Fluorides	2.9 mgL^{-1}	Zinc	<0.005 Zn mgL^{-1}
Calcium	93 Ca mgL^{-1}	Oxygen and organic matters	
Chlorides	420 Cl mgL^{-1}	Dissolved oxygen	1.4 mg O$_2$L^{-1}
Magnesium	9.4 Mg mgL^{-1}	Oxidable atmospheric KMnO$_4$	1.2 mg O$_2$L^{-1}
Potassium	22 K mgL^{-1}	Parameters of nitrates and phosphates	
Soluble silicones (in SiO$_2$)	12.0 mg SiO$_2$L^{-1}	Ammonium	0.11 mg NH$_4$L^{-1}
Sodium	440 Na mgL^{-1}	Nitrates	1.4 mg NO$_3$L^{-1}
Sulphates	450 mg SO$_4$L^{-1}	Nitrites	1.4 mg NO$_2$L^{-1}
Iron and Manganese		Orthophosphates	1.4 mg PO$_4$L^{-1}

Results and discussion. The first stages of the study consisted in the evaluation of corrosion activity in the pipeline – mineral water system performed by the analysis of the polarization curves for the base and the weld metals in the mineral water and the demineralized water. The tests were carried out in the conditions when the solution was open to the atmosphere ($C_{O_2} = 7.9…8.1$ ppm). The most general observation obtained from this study is as follows. The 316L steel and its weld are electrochemically active in the given environments because the typical passive region (plateau) on anodic polarization curves are practically absent (Fig. 4). The mineral water demonstrates a significantly higher corrosive aggressiveness to compare with the demineralized water and the sensitivity to corrosion can be expected for a considered pipeline.
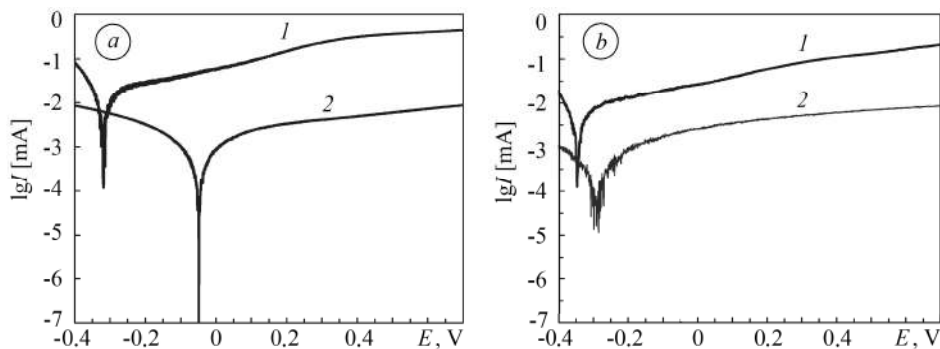

Fig. 4. Potentiodynamic polarization curves for base metal (*a*) and weld metal (*b*) in the mineral water (*1*) and the demineralized water (*2*).

In this case, it is very important to evaluate the role of oxygen in the corrosion process for the given material–environment system. With this aim, the potentiodynamic polarization curves for the base and weld metals under different oxygen concentration in the mineral water were received. Based on these data the corresponding values of corrosion potential E_{corr} and corrosion current I_{corr} were determined as a function of oxygen concentration C_{O_2} in the environment (Fig. 5).
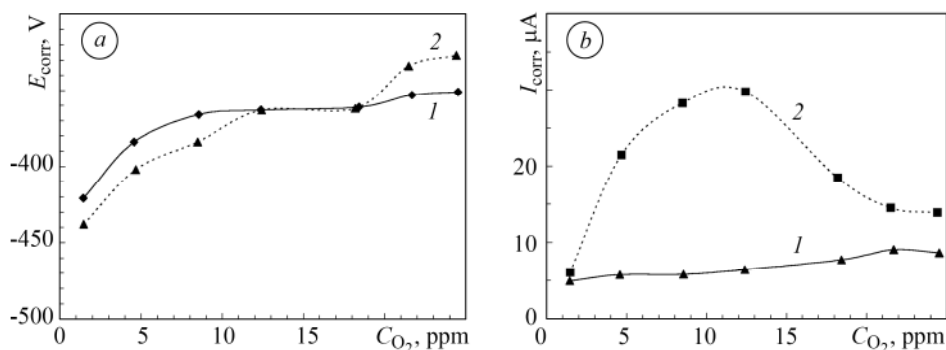

Fig. 5. Dependences of corrosion potential E_{corr} (*a*) and corrosion current I_{corr} (*b*) for the base metal (*1*) and the weld metal (*2*) on oxygen concentration C_{O_2} in the mineral water.

These results demonstrate the significant oxygen effect on the basic corrosion parameters E_{corr} and I_{corr}. In general, the values of corrosion potential E_{corr} increase monotonically (become more positive) for both the base and weld metals with increasing oxygen concentration C_{O_2} (Fig. 5*a*). However, some plateau (stabilisation) of these values can be observed within the range 8 ppm $\leq C_{O_2} \leq$ 18 ppm. In general, the shift of the corrosion potential value E_{corr} to positive values is equal to more than 100 mV when the oxygen concentration in solution increases from 1.5 ppm to 24.5 ppm.

For the values of corrosion current I_{corr} this trend is different for the base metal and the weld metal (Fig. 5*b*). For the base metal within the range 1.5 ppm $\leq C_{O_2} \leq$ 24.5 ppm of the oxygen concentration increase the values of corrosion current I_{corr} increase monotonically from 5 to 8 µA. This increase can be considered as not very significant. For the weld metal, the oxygen effect on the corrosion current values I_{corr} is significantly higher. Besides, dependence $I_{corr} = f(C_{O_2})$ is non-monotonic and achieves the maximum at $C_{O_2} \cong$ 10 ppm. Here the corrosion current value I_{corr} is in 6 times higher than at $C_{O_2} = 1.5$ ppm (Fig. 5*b*, curve *2*). It should be noted that this critical point $C_{O_2} \cong$ 10 ppm is very close to the conditions when the solution is open to the atmosphere ($C_{O_2} = 7.9\ldots8.1$ ppm), i.e. to the real operation conditions of the given pipeline. This fact explains the existence of numerous corrosion damages at the pipeline welded joints (see Fig. 1*b*).

As a summary of this stage, it can be concluded that the pipeline–mineral water system is a corrosive active system and the oxygen concentration in the environment plays a very important though controversial role. The second stage of the study is devoted to the research of some possible ways to reduce the pipeline corrosive activity. In this case, we can not affect the mineral water composition because it is the product for the end user.

As it is known from literature [12] the formation of the passive protective layer on the internal surfaces of the pipeline is a simple and effective way to improve the corrosion resistance. As a first attempt, we used the specimen surface treatment with the 20% aqueous solution of the nitric acid (HNO_3) as it was made in paper [13]. The result of this trial was negative because the specimen surface after such treatment became more corrosive active (see Fig. 6). In addition, that way probably was not acceptable because of the possible effect on a human body, because the given pipeline network was used for supplying the mineral water to the swimming pools.
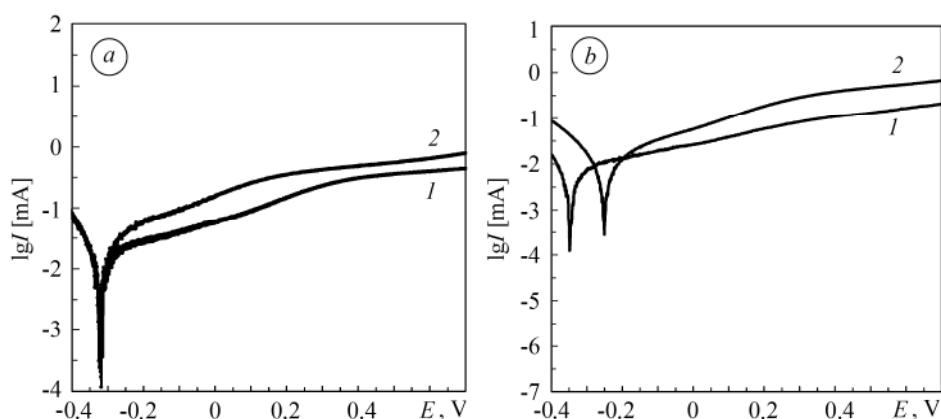
Fig. 6. Potentiodynamic polarization curves of the base metal (*a*) and the weld metal (*b*) in the mineral water after exposure of the specimens during time τ to 20% HNO_3 aqueous solution: *1* – $\tau = 0$; *2* – $\tau = 0.67$ h.

Taking into account this circumstance we tried to find the "safe" solution that was based on the use of the demineralized water for the passive films formed on the internal surfaces of the pipeline.

To prove this suggestion the testing of the specimens with preliminary treatments (see Table 3) were carried out and the potentiodynamic polarization curves for the base and the weld metals at different oxygen concentration in the mineral water were obtained. These data served as a basis for determining the dependences $E_{corr} = f_i(C_{O_2})$ and $I_{corr} = f_j(C_{O_2})$ for three states of the specimen surfaces according to Table 3. The received results showed the visible effect of the preliminary treatment of specimens on the corrosion behaviour of the base (Fig. 7*a*, *b*) and the weld (Fig. 7*c*, *d*) metals.

Table 3. Preliminary treatments of the specimens before electrochemical tests of the base and the weld metals of the 316L steel in mineral water

No	State of specimens surface
1	As-received (without any preliminary treatment)
2	Preliminary exposure to the demineralized water for time $\tau = 40$ h ($C_{O_2} \cong 9$ ppm)
3	After preliminary exposure of the specimens to the demineralized water saturated with oxygen for time $\tau = 90$ h ($C_{O_2} \cong 28$ ppm)

Preliminary exposure of specimens to the demineralized water gives some positive effect on the corrosion potential E_{corr} for the base metal (Fig. 7*a*, curve *2*) and the weld metal (Fig. 7*c*, curve *2*) in comparison with the non-treated specimens. However, the strongest effect can be observed for the specimens subjected to preliminary exposure to the demineralized water saturated with oxygen (Figs. 7*a*, *c*, curves *3*). In this case, the shift of the corrosion potential values E_{corr} to positive ones is equal to more than 400 mV when the oxygen concentration in solution increases from 1.5 ppm to 24.5 ppm.

The similar fact can be observed for the values of the corrosion current I_{corr} (Figs. 7*b*, *c*). The preliminary exposure of the specimens to the demineralized water saturated with oxygen leads to a significant decrease of the corrosion current for the base metal as well as for the weld metal. Especially this effect is clearly seen for the weld metal where the maximum on the dependence $I_{corr} = f_j(C_{O_2})$ disappears (Fig. 7*c*, curve *3*) in comparison with the non-treated specimens (Fig. 7*d*, curve *1*). It should also be marked that for this case the change of the values I_{corr} is quite small with increasing

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oxygen concentration in the mineral water within the range 1.5 ppm $\leq C_{O_2} \leq$ 24.5 ppm. This result is very important because it confirms the fact of the existence of the passive protective film on the specimen surface, which is created during the preliminary treatment of specimens with the oxygen-saturated demineralized water.
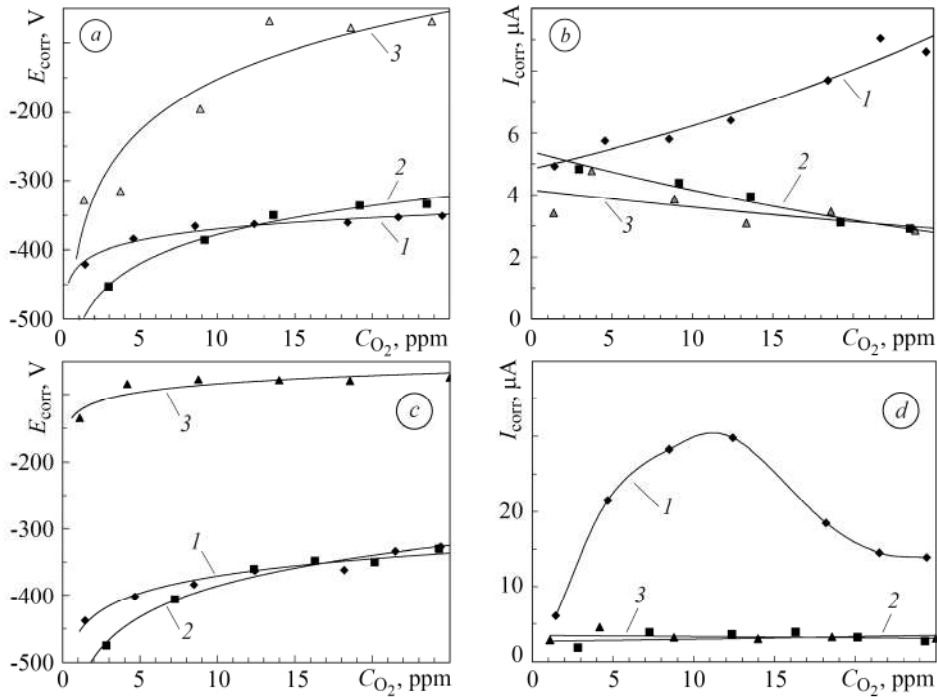

Fig. 7. Dependences of corrosion potential E_{corr} (a, c) and corrosion current I_{corr} (b, d) for the base metal (a, b) and for the weld metal (c, d) on oxygen concentration C_{O_2} in the mineral water for the different stats of the specimens surface: 1 – as-received; 2 – after preliminary exposure to the demineralized water (τ = 40 h); 3 – after preliminary exposure to the demineralized water saturated with oxygen (τ = 90 h).

Therefore, it can be concluded that for the given case the demineralized water saturated with oxygen can serve as an effective preliminary tool for improving the corrosion resistance of the internal surface of the 316L steel pipeline for the mineral water transportation.

The final stage of this study shows the transformation of the polarization curves of the base and the weld metals in the mineral water as a result of preliminary exposure of specimens for time τ to demineralized water saturated with oxygen. This is important for development of the practical recommendations on the optimal time of the preliminary treatment of the considered pipeline internal surface.

In general, any preliminary exposure of the specimens to the demineralized water saturated with oxygen leads to the appearance of the passive region (plateau) on the anodic polarization curves of the base (Fig. 8a) and weld (Fig. 8b) metals in the mineral water. It can be seen clearly when comparing curves 2–5 with curve 1 in Fig. 8.

This trend can be analyzed using two parameters, namely: length of the plateau ($\Delta E_{plateau}$) and current at the plateau ($I_{plateau}$). The last parameter was determined as the anodic current at $E = 0$ because point $E = 0$ was always located on the plateau for all considered cases. The numerical values of parameters $\Delta E_{plateau}$ and $I_{plateau}$ are given in Table 4.

The obtained results show (Table 4) that the length of plateau $\Delta E_{plateau}$ increases with increasing time of exposure and this parameter can achieve the value of 310 mV after exposure time τ = 21.25 h for the base metal and the value of 400 mV after expo-

sure time $\tau = 23.5$ h for the weld metal. At the same time parameter $I_{plateau}$ decreases significantly with increasing time of exposure and this tendency reflects the growth of the corrosion resistance of the specimen surface. Based on the obtained data it can be concluded that optimal time of the welded pipe preliminary treatment is equal to about 24 h.
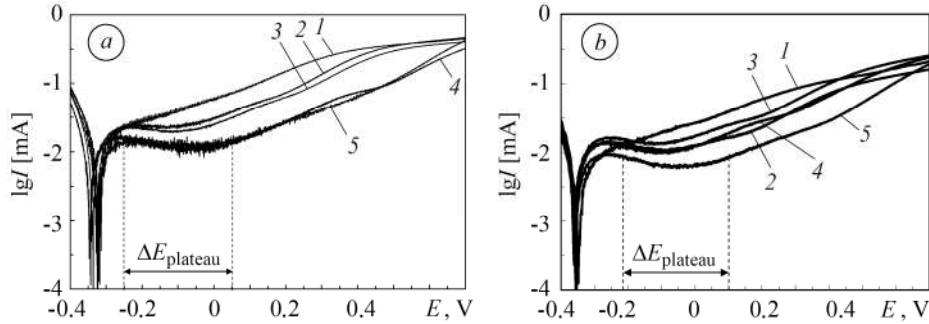

Fig. 8. Polarization curves of the 316L stainless steel (*a*) and weld (*b*) metals in the mineral water after exposure for time τ of the specimens to demineralized water saturated with oxygen:
a: *1* – τ = 0; *2* – τ = 0.25 h; *3* – τ = 0.5 h; *4* – τ = 21.25 h; *5* – τ = 66.25 h;
b: *1* – τ = 0; *2* – τ = 0.5 h; *3* – τ = 1 h; *4* – τ = 3 h; *5* – τ = 23.5 h.

**Table 4. Basic parameters for evaluation of the electrochemical behaviour
of the welded 316L stainless steel in the mineral water**

Time of exposure τ, h	Length of passive plateau $\Delta E_{plateau}$, mV	Current at plateau $I_{plateau}$, mV
Base metal		
Preliminary exposure of the specimens to the demineralized water saturated with oxygen		
0	0	0.0590
0.25	140	0.0300
0.50	200	0.0250
21.25	310	0.0120
66.25	310	0.0120
Preliminary exposure of the specimens to the demineralized water saturated with oxygen under anodic polarization at $I_a = +0.020$ mA		
0	0	0.0590
0.50	400	0.0310
1.25	440	0.0190
18.6	460	0.0100
Weld metal		
Preliminary exposure of the specimens to the demineralized water saturated with oxygen		
0	0	0.0268
0.5	200	0.0125
1	200	0.0122
3	307	0.0124
23.5	400	0.0067
Preliminary exposure of the specimens to the demineralized water saturated with oxygen under anodic polarization at $I_a = +0.020$ mA		
0	0	0.0268
0.5	395	0.0073
1	390	0.0101
3	380	0.0082
233.75	500	0.0065

For strengthening of the positive effect of the specimens preliminary exposure to the demineralized water saturated with oxygen, the small anodic current can be applied simultaneously. This leads to the acceleration of the process of the passive film formation on the surface. The results, which are given in Fig. 9, can serve as some confirmation of this statement. Here the additional application of the anodic polarization current $I_a = +0.020$ mA increases the length of the plateau up to a value of 460 mV for the base metal. The similar trends are observed also for the welded joints of the 316L steel where the length of the plateau can reach a value of 500 mV (see Table 4).
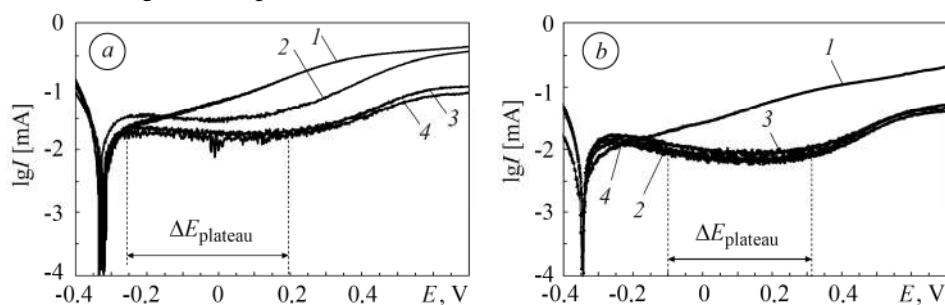

Fig. 9. Polarization curves of the 316L stainless steel (*a*) and weld (*b*) metals in the mineral water after exposure for time τ of the specimens at anodic polarization current $I_a = +0.020$ mA to the demineralized water saturated with oxygen: *a*: *1* – $\tau = 0$; *2* – $\tau = 0.5$ h; *3* – $\tau = 1.25$ h; *4* – $\tau = 18.6$ h; *b*: *1* – $\tau = 0$; *2* – $\tau = 0.5$ h; *3* – $\tau = 1.0$ h; *4* – $\tau = 3.0$ h; *5* – $\tau = 233.75$ h.

It should be noted that sometimes is not possible to introduce the anodic current into the pipeline system because of its different nature: technical, economical, medical, ecological, etc. Therefore, the application of this method needs further justification depending on the actual situation.

CONCLUSIONS

The comparative assessment of the sensitivity to corrosion of the 316L stainless steel welded pipe in the mineral water was made under different electrochemical conditions. For a considered case this steel demonstrates an unusual electrochemical behaviour and the typical passive region on the anodic polarization curve is practically absent. Therefore the steel is electrochemically active in the given environment that causes its sensitivity to corrosion. It should also be pointed out that the value of oxygen concentration in mineral water plays a very important role in providing the passive (non-corrosive) state of the pipeline system during operation.

It has been shown that the preliminary exposure of the specimens to the demineralized water saturated with oxygen leads to the passive region (plateau) appearance on the anodic polarization curve of steel and its weld in the mineral water. The length of this plateau $\Delta E_{\text{plateau}}$ increases with increasing exposure time and this parameter can reach a value of 310 mV after exposure time $\tau = 21.25$ h for the base metal and a value of 400 mV after exposure time $\tau = 23.5$ h for the weld metal. Under these conditions, the additional application of the anodic polarization current $I_a = +0.020$ mA increases the length of the plateau up to a value of 460 mV. The similar trends are observed also for the welded joints of 316L steel ($\Delta E_{\text{plateau}} = 500$ mV). It can be concluded that the given 316L steel pipeline requires preliminary treatment before using for transportation of the mineral water and the demineralized water saturated with oxygen and can serve as an effective preliminary tool for improving the corrosion resistance of the internal surface of the pipeline for the mineral water transportation. The optimal time of preliminary treatment of the welded pipe is equal to about 24 h. The proposed study illustrates the environmental conditions, which simulate the real operation of the pipeline and therefore the obtained results may be used as reference data preventing corrosion damaging of the pipeline and improvement of its serviceability in such specific conditions.

РЕЗЮМЕ. Порівняльно оцінено чутливість до корозії труби з нержавкої сталі 316L та її зварних з'єднань у мінеральній воді за різних електрохімічних умов. У цих умовах сталь демонструє незвичну електрохімічну поведінку і типова пасивна область на анодній поляризаційній кривій практично відсутня, тобто вона електрохімічно активна в даному середовищі, а отже, чутлива до корозії. Встановлено, що попередня витримка зразків у демінералізованій воді, насиченій киснем, призводить до утворення пасивної області (плато) на анодній поляризаційній кривій сталі в мінеральній воді. Довжина цього плато значно зростає зі збільшенням часу експозиції і за додаткового прикладання струму анодної поляризації. Аналогічні тенденції зафіксовано і для зварних з'єднань цієї сталі. Запропоновано вид обробки внутрішньої поверхні трубопроводу перед його використанням для транспортування мінеральної води.

РЕЗЮМЕ. Осуществлена сравнительная оценка чувствительности к коррозии трубы из нержавеющей стали 316L и ее сварных соединений в минеральной воде в различных электрохимических условиях. В данных условиях сталь демонстрирует необычное электрохимическое поведение и типичная пассивная область на анодной поляризационной кривой практически отсутствует, т.е. она является электрохимически активной в данной среде, а, следовательно, чувствительна к коррозии. Установлено, что предварительная выдержка образцов в деминерализованной воде, насыщенной кислородом, приводит к образованию пассивной области (плато) на анодной поляризационной кривой стали в минеральной воде. Длина этого плато значительно возрастает с увеличением времени экспозиции и при дополнительном приложении тока анодной поляризации. Аналогичные тенденции зафиксированы и для сварных соединений этой стали. Предложен вид обработки внутренней поверхности трубопровода перед его использованием для транспортировки минеральной воды.

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