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STEEL C15E CORROSION RESISTANCE TO DISINFECTANTS

The article presents a comparative analysis of the corrosiveness of chlorine-containing disinfectants such as sodium hypochlorite, calcium hypochlorite and chlorinated lime, and a saturated solution of ozone in water to carbon steel C15E. Investigations have been carried out by weight and indirect electrochemical method, i. e. the Zomelfeld method. The description of the applied methods of the research and the composition of the investigated steel are presented. To determine the resistance band of the metal in relation to the solution of various concentrations the weight and deep coefficient of corrosion rate has been calculated. The physical and chemical processes occurring on the surface of the metal in the treated environment are described. It was found that the most corrosive test solution is the saturated solution of ozone in water, and the most corrosive chlorine disinfectant is sodium hypochlorite. Calculated on the current density weight and depth corrosion indicators of steel C15E in disinfectant solutions are in the 2–17 times higher than those obtained in the test weight. It is noted that for the disinfection of water supply facilities and water wells through a substantially shorter processing time by ozone in comparison with chlorine-containing reagents weight corrosion rate using ozone is significantly less than the minimum corrosion rate when using chlorine-containing reactants.

Key words: corrosion, sodium hypochlorite, calcium hypochlorite, bleach, ozone.

Introduction. Casing by a casing is made to strengthen the borehole walls from collapse. Metal (galvanized, stainless steel, enameled), asbestos cement or polymeric (PVC, HDPE) casing are used for this purpose depending on the well parameters and destination. These products are divided into technical and drinking. Recently, the most widely used in drilling water intake wells are PVC casing. In some cases, there are variants for installing a plastic casing inside the metal one.

However, today the vast majority of casing is made of steel. As casing for private water supplies they often use seamless tubes of mild steels such as steels of 15 GOST 8732-78 brand steels.

By virtue of the fact that the disinfecting reagents are strong oxidizers, they are highly corrosive, which leads to rapid wear of the grids and stop valves. Therefore, the choice of method of disinfection should be based not only on the qualitative and quantitative indicators of drinking water, but available reliable information about the effects of chemicals on the materials of water intake facilities and water supply systems.

Today the results of many studies to determine the corrosion of chlorine-containing acid media on metal surface are known [1–3]. According to this research a corrosion rate of chlorine-containing compounds is less than 0.5 cm/year depending on the content of additives in solution, pH, temperature and time of exposure.

On the other hand, when using ozone as a disinfectant it is necessary to compare its corrosiveness with solutions of chlorine disinfectants. Available information on the corrosiveness of the ozone solution in water is very different and it is given for each specific application of ozone. Thus, for example, according to studies [4], the corrosiveness of water ranges from 0.002 to 0.008 mg/cm^2 after ozonation and sorption of water with coagulant. Aluminum sulfate is used as a coagulant. However, there are no systematized experimental data on the corrosiveness of ozone in water of drinking quality without additives, so it is of interest to test the corrosion resistance of steels to disinfectant solutions.

Analyzing information [5] on 15 steel corrosion in various aqueous solutions, we can conclude that today there are no data which can help to analyze in comparable conditions the corrosive effect on materials of water intake wells and water supply facilities containing chlorine disinfectants and dissolved ozone.

Therefore, the aim of the presented work was to determine the corrosion resistance of steel 15 in an aqueous medium containing the tested disinfectants (sodium hypochlorite, bleach, calcium hypochlorite, ozone).

Main part. The following reagents: calcium hypochlorite, sodium hypochlorite, bleaching powder, a saturated solution of ozone in water were used to determine the corrosion resistance of steel 15. Test concentrations of used chlorine disinfectants are 50, 100 and 150 mg/l of active chlorine. For a saturated solution of ozone in the water there used cascade turboozonator company LLC “Rovalant-SPETSSERVIS”, volume of treated water – 200 ml, the concentration of ozone in the gas mixture after the saturation was 2.7 g/m^3, the gas mixture consumption was 13.2 liters/m, the saturation time was 30 min. During the research process the feed of ozone containing gas mixture was not stopped. Mild steel plates from steel grade 15 (the European equivalent S15E) were used for corrosion tests.

Table 1

The elemental composition of the investigated steel of brand steel 15 wt %

C	Si	Mn	Ni	S	P	Cr	Cu	Mg
0.135	0.013	0.433	0.043	0.034	0.015	0.051	0.098	0.0001
Mo	Al	Ti	V	Sn	Pb	Zn	Fe	–
0.002	<0.001	<0.001	0.001	0.004	0.001	<0.001	res.	–

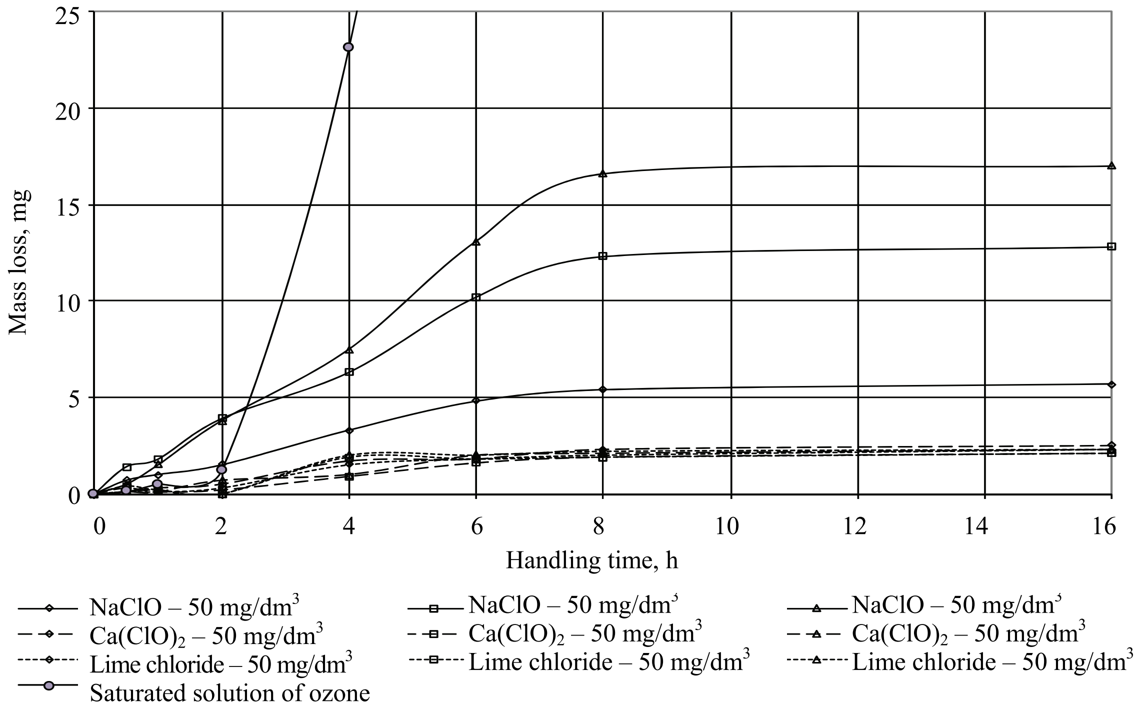

Fig. 1. The mass loss of steel 15 metal plate depending on the time of exposure to disinfectant solution

Casing pipes made of this steel were widely used in drilling water intake wells in the 80–90-ies. Dimensions of the tested steel samples were (20 × 20 × 5) mm.

The research was carried out by weight (direct) and electrochemical (indirect) method (GOST 9.908-85). The potential was measured relatively to the saturated silver chloride reference electrode for 30 min at a room temperature and was converted to the scale of a standard hydrogen potential.

To determine the resistance group of the metal with respect to the disinfectants we have calculated weight (K_m, g/m^2 · h) and depth (K_g mm/year) index of corrosion, which corresponds to a decrease in the thickness of the metal due to corrosion. The group and the severity of metal resistance in this aggressive environment were determined by the value of corrosion depth index.

The elemental composition of steel was determined on spark vacuum optical emission spectrometer (analyzer of metals and alloys) OBLF QSN 750. The accuracy of the elements – 0.001%.

The chemical composition of the steel (Table 1) was previously studied to determine the concentration of the elements enlarging the corrosion rate. The mass content of carbon 0.135 wt % indicates pearlite-ferrite structure of unhardened steel 15 and its increased susceptibility to corrosion due to the presence in the alloy of the two electrochemically dissimilar phases: ferrite and perlite (a mixture of tertiary eutectoid ferrite and cementite). Moreover, the presence of sulfur, copper and phosphorus, respectively, 0.034, 0.098 and 0.015 wt % will facilitate the flow of the corrosion process of iron oxidation with oxygen and hydrogen depolarization. At the first stage the study was performed gravimetrically. As it is seen from the results shown in Fig. 1, mass loss of plates in the tested disinfectant solution takes place uniformly with a decrease in the rate of corrosion over time. In a saturated ozone solution for steel 15 there appears a sharp decrease in the loss of mass of the plate after being 2 hours in the solution.

Virtually no mass change is observed for steel plates immersed in aqueous solutions of sodium hypochlorite, bleach, calcium hypochlorite. The observed phenomenon is associated with the formation of a thick oxide layer, which perhaps leads the corrosion process to the diffusion control.

Table 2

Corrosion depth index of carbon steel of brand steel 15 in disinfectant solutions

The solution	Concentration mg/dm^3	K_m, g/(m^2·h)	K_d, mm/year	Resistance group	Severity of resistance
NaClO solution	50	1.01	1.12	Low resistant	8
	100	1.10	2.35	Low resistant	8
	150	1.95	2.17	Low resistant	8
$Ca(ClO)_2$ solution	50	0.33	0.36	Reduced resistant	6
	100	0.28	0.32	Reduced resistant	6
	150	0.28	0.31	Reduced resistant	6
Bleaching solution	50	0.25	0.28	Reduced resistant	6
	100	0.37	0.42	Reduced resistant	6
	150	0.28	0.31	Reduced resistant	6
Saturated ozone solution		5.56	6.20	Low resistant	9

Table 3

Indicators of corrosion of carbon steel brand steel 15, resistance group and severity in NaCl solutions

Solution	K_m, g/(m^2·h)	K_d, mm/year	Resistance group	Resistance severity
Distilled water	0.08	0.09	Resistant	5
NaCl 1%	0.05	0.06	Resistant	5
NaCl 2%	0.08	0.09	Resistant	5
NaCl 3%	0.3	0.34	Reduced-resistant	6

The corrosion depth index of steel 15 in the disinfectants calculated by the received experimental data is presented in Table 2. According to the resistance severity steel 15 in ozonated water is low corrosion resistant with corrosion depth index of 6.2 mm/year, which makes this steel unsuitable for constructive purposes. For solutions of sodium hypochlorite, this indicator is in the range of 1.12 to 2.17 mm/year. At the same time the index of the corrosion depth of steel 15 in solutions of bleach and calcium hypochlorite is less than 0.42 mm/year, but this steel is considered to be reduced-resistant steel and can be applied using a special anti-corrosion protection.

To determine the corrosion resistance of steel 15 to the saturated ozone solution in water we made additional study in 1, 2 and 3 wt % solutions of NaCl (Table 3) in order to increase its conductivity.

In the absence of strong oxidants (active chlorine, ozone) corrosive dissolution of steel 15 occurs uniformly with possible self-passivation of the surface. The value of the corrosion depth index does not exceed 0.09 mm/year, which corresponds to the resistant metals. However, the increase in the salt concentration up to 3 wt % leads to the indicator growth to 0.34 mm/year and the decrease in the corrosion resistance of steel 15. This is probably due to the growing process of dissolution of the oxide-hydroxide layer on the steel surface by complex-formation with an increase in the concentration of chloride-ions.

The rate of corrosion of steel 15 in aerated distilled water is also quite large (0.09 mm/year), due to non-uniform structure of the alloy. The presence of separate phase of ferrite and perlite in the steel 15 generates electrochemical irregularities on the plate surface and promotes the formation of short-circuited corrosive elements in which ferit is an anode and perlite is a cathode.

Indirect studies of steel 15 corrosion in disinfectant solutions were made by electrochemical method (Zomelfeld). The results of the electrochemical tests are presented in Table 4.

Calculated on current densities the weight and depth corrosion indexes of steel 15 in disinfectant solutions are in 2–17 times higher than those obtained in the weight tests. Primarily, the differences are due to surface roughness during electrochemical measurements and intercrystalline corrosion which are not determined in weight tests. However, according to the results of the electrochemical tests steel 15 in aqueous solutions of bleach and calcium hypochlorite is reduced resistant but in ozone solution and sodium hypochlorite solution it is low-resistant or unstable, which is consistent with previous data obtained by the gravimetric method.

Of particular interest is the study of the process of corrosion of steel 15 in the water saturated with ozone, in which there is a rapid rate of dissolution of iron with more than 96 mm/year due to the high oxidizing activity of ozone.

Table 4

The depth and the weight corrosion index of carbon steel brand Steel 15 in disinfectant solutions determined by the electrochemical method

Solution	Concentration mg/dm^3	i_{corr}, mA/cm^2	K_m, g/(m^2 · h)	K_d, mm/year	Resistance group	Resistance severity
Solution NaClO	50	1.669	17.44	19.59	Unstable	10
	100	1.219	12.74	14.31	Unstable	10
	150	0.344	3.59	4.04	Low resistant	8
Solution $Ca(ClO)_2$	50	0.015	0.16	0.18	Reduced-resistant	6
	100	0.054	0.56	0.63	Reduced-resistant	7
	150	0.063	0.66	0.74	Reduced-resistant	7
Bleach	50	0.086	0.90	1.01	Reduced-resistant	7
	100	0.113	1.18	1.33	Low resistant	8
	150	0.111	1.16	1.30	Low resistant	8
Saturated ozone solution		8.258	86.29	96.93	Unstable	10

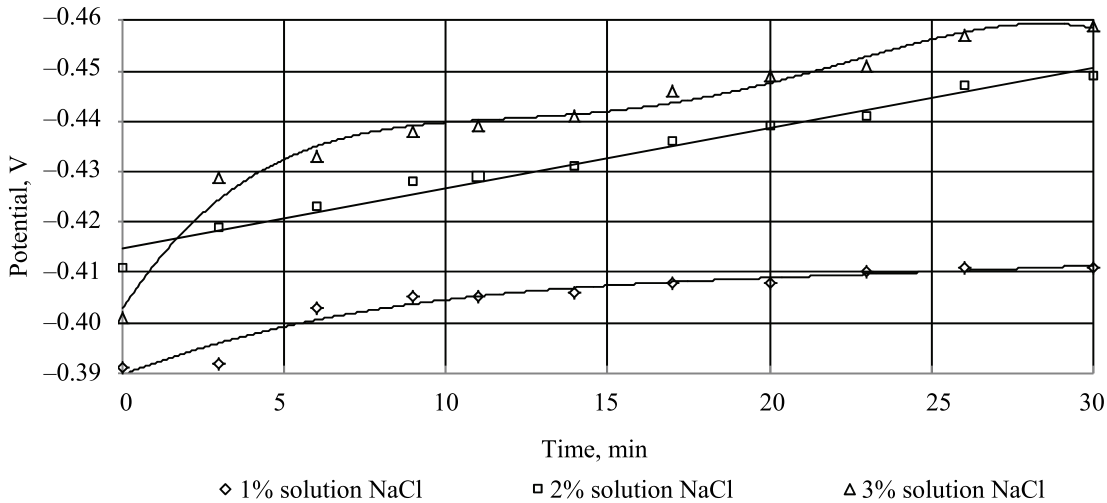

Fig. 2. Steel 15 potential in ozonized water depending on exposure time

Chronopotentiogram of the process of steel 15 corrosion is shown in Fig. 2.

Fig. 2 shows that with the increase in exposure time of steel 15 in the water saturated with ozone from 5 to 30 minutes there occurs a potential shift for all tested solutions by 10–30 mV to electronegative side. Thus, the passivation of steel 15 surface is not observed, since ozone is most likely to oxidize the iron to Fe^{+3} in one step, avoiding the formation process of a dense passivation film FeO.

In its turn, the presence of Fe^{+3} and its metahydroxide on the surface multiply increases the speed of the corrosion process.

Increasing the concentration of chlorides in the ozonised water also accelerates the corrosion process, which is most likely due to the catalytic action of specifically adsorbed chloride ions on the iron surface.

Conclusion. According to the obtained results steel 15 in ozone saturated water is low resistant with the depth corrosion index of 6.2 mm/year (according to the weight tests). For solutions of sodium hypochlorite this Figure is in the range of 1.12 to 2.17 mm/year but in the bleach and calcium hypochlorite solutions it doesn't exceed 0.42 mm/year. Electrochemical tests also indicate low resistance or instability of steel 15 in ozonized water and sodium hypochlorite solution, but in solutions of bleach and calcium hypochlorite this steel is reduced resistant. It should be noted that the processing time of water intake boreholes with chlorinated reagents is about 24 hours but by their treatment with ozone it is about 20 minutes. Wherein the weight corrosion indicator in water saturated with ozone will be in 13.1–25.3 times less than the minimum weight indicator of corrosion when using sodium hypochlorite, in case of calcium hypochlorite it is less in 3.6–4.3 times, if bleach is used it is less in 3.2–4.8 times.

In the absence of strong oxidants (active chlorine, ozone) corrosion dissolution of steel 15 occurs uniformly with self-passivation of the surface.

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