*Досліджений вплив гідроксиду натрію на швидкість і характер корозії чорних металів у мінералізованій оборотній воді. Показано, що гідроксид натрію є ефективним інгібітором корозії вуглецевої сталі Ст3 і сірого чавуну СЧ 18–36. За результатами гравіметричних та поляризаційних досліджень визначений характер руйнування, розрахований ваговий показник швидкості корозії і електрохімічні параметри зазначених матеріалів у оборотній воді*

*Ключові слова: оборотні води, корозія, вуглецева сталь, сірий чавун, мінералізація, гідроксид натрію*

*Исследовано влияние гидрооксида натрия на скорость и характер коррозии черных металлов в минерализованной оборотной воде. Показано, что гидрооксид натрия является эффективным ингибитором коррозии углеродистой стали Ст3 и серого чугуна СЧ 18–36. По результатам гравиметрических и поляризационных исследований определен характер разрушения, рассчитан массовый показатель скорости коррозии и электрохимические параметры указанных материалов в оборотной воде*

*Ключевые слова: оборотные воды, коррозия, углеродистая сталь, серый чугун, минерализация, гидрооксид натрия*

# THE STUDY OF INHIBITING STRUCTURAL MATERIAL CORROSION IN WATER RECYCLING SYSTEMS BY SODIUM HYDROXIDE

**A. Pilipenko**
PhD
Department of technical electrochemistry*
E-mail: opilipenko1984@gmail.com

**H. Pancheva**
PhD, Assistant
Department of labor and environment protection*
E-mail: panchevaana@mail.ru

**G. Reznichenko**
PhD
Department of occupational, technogenic and environmental safety**
E-mail: reznichenko@nuczu.edu.ua

**O. Mirgorod**
PhD, Associate Professor
Department of fire prevention in settlements**
E-mail: mir-oksa@ukr.net

**N. Miroshnichenko**
PhD, Associate professor
Chair of integrated technologies, processes and devices*
E-mail: d_tasha@ukr.net

**A. Sincheskul**
PhD
Department of chemical technology of inorganic substances, catalysis and ecology*
E-mail: als-train@ukr.net
*National Technical University «Kharkiv Polytechnic Institute»
Kyrpychova str., 2, Kharkiv, Ukraine, 61002
**National University of civil protection of Ukraine
Chernyshevska str., 94, Kharkiv, Ukraine, 61023

## 1. Introduction

Circulating cooling water is process water repeatedly used in manufacturing operations of periodic heating and cooling, in heat exchangers of metallurgical and chemical industry enterprises [1]. Minimal corrosive effect of recycled water on equipment, pipelines, pumps and structures is a crucial requirement [2].

In the course of water use at plants, its mineralization often grows causing an increase in its corrosivity [3, 4]. Therefore, circulating water is periodically discharged to sewage systems or partially replaced with fresh water. This is not advisable since water volumes consumed by large enterprises can be hundreds of thousands or even millions of cubic meters [3, 5]. Creation of closed-loop cycles enabling multiple use of water is the current topical issue [3]. The problems of corrosion resistance of structural materials in low-mineralized circulating water are given high attention [1].

## 2. Literature review and problem statement

Ferrous metals are main structural materials of recirculating water supply systems [3]. Some equipment parts (locking equipment, pumps, heat exchangers, etc.) are manufactured of non-ferrous metal based alloys: brass, bronze, titanium. Hence the interest paid to corrosive behavior of ferrous metals in circulating systems is explainable.

The main factors affecting metal corrosion rate in recycled water include chemical composition of water [3],

its mineralization [6], quantity of dissolved gases [7], temperature and pH [8], flux velocity, metal surface condition [9]. However, water corrosiveness probably depends on numerous unaccounted factors including presence of impurities in water which cannot be determined by conventional chemical analysis.

Typical conditions determining corrosion of the circulating system equipment are as follows:

1) spray cooling of water circulating in cooling towers contributes to its saturation with oxygen. The circulation participating in this process facilitates good oxygen intake to the metal surface. As a result, favorable conditions are created for proceeding corrosion with oxygen depolarization [1, 5];

2) due to water evaporation in cooling units, concentration of salts grows in the cooling water accompanied by an increase in its aggressiveness. In addition, recycled water can be contaminated with the impurities specific to concrete industries: petroleum [2, 6], coke by-product chemistry [5], metallurgy [3];

3) heat transfer surfaces are made of various metals and the temperature gradient is not uniform in different cycle locations [4];

4) the corrosion process is associated with the phenomena of thermal stability and biogeneity [10, 11].

A special effect of the last two factors on corrosiveness of recycled water should be noted. Carbonate deposits and the action of microorganisms often cause ineffectiveness of the methods used in corrosion protection of circulating water supply systems [10]. Deposits of calcium and magnesium carbonates protect metal from corrosion but their thick layers on the metal surface worsen heat transfer [4].

Biological fouling reduces heat exchange rate in cooling equipment, decreases water pipe throughput capacity and pollutes the recycled water due to dying off microorganisms and deposition of their particles [12, 13]. Moreover, the changes in temperature conditions, water flow velocity and chemical composition affect electrochemical corrosion [5].

Reduction in corrosion rate of the structural materials used in water recycling systems is achieved either through pretreatment of water [3] or introduction of corrosion inhibitors [5]. The purpose of water pretreatment consists in as complete as possible removal of dissolved oxygen and hardening salts. Depending on their type, inhibitors retard anodic or cathodic reaction of electrochemical corrosion. The use of inhibitors is a fairly economical and effective way of metal protection.

In neutral aqueous solutions, black metals are protected by addition of oxidizer-passivators: salts of chromic or nitrous acid [3]. Toxicity is a serious disadvantage of nitrites and especially of chromates and bichromates.

Mono-, twice- and triple-substituted phosphates [9] and polyphosphates [5] have found a rather wide-spread application as corrosion inhibitors. Their advantages include nontoxicity, availability, cheapness, as well as the possibility of preventing formation of carbonate deposits. However phosphate inhibitors cause intensive development of algae in recycled water which brings about increase in intensity of equipment biofouling.

Use of inhibitors based on compositions of organic substances, e.g. modified phosphorus-containing substances [6], organic phosphonates [7], water-soluble polymers [8] is promising. Disadvantage of the composition based on sodium and potassium salts of a mixture of hexanoic and ethylhexanoic acids proposed in [6] is the difficulty in obtaining an inhibitor of a constant composition. This explains the scatter of the experimental data demonstrating its effectiveness. The substance used by the authors of work [7] was salt of 1-hydroxyethylidene diphosphonic acid with 2-dimethylaminomethylphenol (OMED complexon). As the authors themselves point out, this substance is not produced on an industrial scale but is obtained by an experimental synthesis. In addition, this inhibitor effectively works only together with zinc sulfate introduction of which into recycled water leads to appearance of an undesirable heavy metal ion in water. Inhibiting properties of such substances as sulfonated oligomers (naphthalene formaldehyde and melamine formaldehyde), lignosulfonates, sodium salts of polyacrylic acid, polyhexamethyleneguanidine phosphate (anavidin) were studied in [8] but these substances are carcinogens and poorly decompose under natural conditions. A common drawback of organic inhibitors is their high cost. This is especially evident in processing circulating water the volumes of which can measure millions of cubic meters.

Therefore, it is promising to search for substances that can simultaneously possess the following properties: significant reduction of ferrous metal corrosion rate, prevention of development of microorganisms and algae, cheapness and affordability. Sodium hydroxide (NaOH) can be such substance, a common and rather cheap product of the chemical industry. In addition, NaOH has bactericidal properties [6]. The possibility of using the same substance for simultaneous corrosion protection and suppression of biofouling has determined course of the studies undertaken in this work.

## 3. Objective and tasks of the study

This work objective consisted in the development of a new method of corrosion protection of equipment for recycling water supply systems based on the hypothesis of relationship between corrosion rate of ferrous metals and water pH.

To achieve this objective, the following tasks were set:

– to determine effect of the circulating water composition on the nature and rate of corrosion of carbon steel St3 and gray cast iron SCh 18–36 in circulating mineralized water;

– todetermine main electrochemical characteristics of carbon steel St3 and gray cast iron SCh 18–36 depending on composition and pH of the corrosive medium.

## 4. Procedure of studying corrosion of gray cast iron and carbon steel in circulating mineralized water

Samples for gravimetric testing were prepared according to the generally accepted scheme [14]. The samples were sanded with emery or polishing paper and polished with a felt wheel. The polished samples were degreased with an alkaline solution, washed with distilled water and dried with filter paper. Samples were suspended on glass hooks and immersed in 1-liter flasks with a corrosive medium. To maintain constant temperature of the solutions, the flasks were installed in 5-liter crystallizers filled with tap water. The tests were carried out on polished samples made of carbon steel St3 with dimensions of 40×25×3 mm and grey cast iron SCh 18–36 with diameter of 30 mm and thickness of 2–3 mm. Duration of the tests was 1,560 h, solution temperature was 22 °C. The solution pH was monitored every 24 hours and corrected

if necessary. Weight loss of the samples was determined by weighing them with ANG 200 scale. The nature of metal corrosion damage was assessed visually with a 8–12 magnifying glass. Pattern of corrosion, its weight index $k_w$, $g \cdot (m^2 \cdot h)^{-1}$, and the protective effect $Z$ (%) were determined in the tests.

Electrochemical tests were carried out by plotting polarization dependences using the IPC-PrO potentiostat. The study cell was a U-shaped glass vessel in which anode and cathode spaces were separated by a glass diaphragm.

Platinum was used as an auxiliary electrode. Electrode potentials were measured relative to the silver chloride reference electrode. Cylindrical samples of St3 grade steel and SCh 18–36 grade cast iron having diameter and length of 10 mm were used in the studies. The sample end face was taken as the work surface.

Samples were ground with sandpaper with a gradual transition to smaller paper grain sizes. After grinding, the samples were mechanically polished using chromium paste. The polished electrodes were degreased with an aqueous alkaline solution, washed with water and dried with filter paper. Before experiments, the samples were kept in solution for 30 minutes. The currents in the potentiostatic polarization dependences were fixed after holding the electrode at a specified potential for 5 minutes. As a result of polarization measurements, stationary potential $E_{st}$, pitting potential $E_{pit}$, region of passive state $\Delta E$ of the studied samples were determined.

## 5. Results obtained in the corrosion studies of St3 steel and SCh 18–36 cast iron in circulating mineralized water

One of the most important factors affecting corrosion of metal is the solution pH. Metal applicability is often determined in practice by the pH values within which it is satisfactorily resistant. As a rule, the circulating water is maintained in practice between pH figures 6 and 8 [1].

The rate of corrosion of iron in the alkaline range of pH slows down [14, 15]. However, these data relate either to non-mineralized solutions or to the studied solutions for which pH was maintained with the use of a universal buffer mixture containing a phosphate ion as an inhibitory component.

Therefore, it is of interest to study the protective effect of NaOH on structural materials of circulating systems working with mineralized water. Availability of using sodium hydroxide is determined by its low cost advantageously distinguishing it from most of the non-cheap and often toxic corrosion inhibitors. An additional reason for using NaOH is that it possesses a property of suppressing bacteria and algae development [13]. Therefore, the same reagent can used both for protection against corrosion and for suppression of biofouling.

An increase in the circulating water pH associated with addition of NaOH may lead to an intensification of the salt deposition process. However, when working with highly mineralized recycled water, the system is sufficiently fed with condensate, that is the water containing no additional amounts of hardness salts. Sometimes circulating cycles are

fed not by river water but by purified water containing up to $2\,g\,l^{-1}$ NaCl and having total hardness up to $1.5$–$2\,(mg \cdot eq)\,l^{-1}$.

Thus, in production conditions, feeding the system with water containing a minimum amount of hardness salts will make it possible to avoid the problem of salt deposits even at alkaline values of the recycled water pH.

The assumption of using NaOH to suppress corrosion in circulating water requires laboratory testing. This is necessary to determine concrete conditions under which the corrosion rate will correspond to the permissible values i.e. under $0.1\,g \cdot (m^2 \cdot h)^{-1}$ [5].

The results of pH effect on the rate of corrosion of carbon steel and gray cast iron in recycled water with mineralization of 0.02 M are given in Table 1. The test duration was 1,560 h at 22 °C.

As can be seen from the data in Table 1, when solution pH increases to 13, the rate of metal corrosion decreases significantly, especially in the waterline zone (5 to 8 times). Obviously, this is due to formation of insoluble protective films directly retarding the anodic dissolution process at alkaline pH values.

Table 1

Effect of pH on the rate of corrosion of carbon steel and grey cast iron in recycled water containing 0.02 M NaCl

| Material | pH | Test location | $k_m$, $g \cdot (m^2 \cdot h)^{-1}$ | Corrosion pattern |
|---|---|---|---|---|
| Steel St3 | 8 | in electrolyte | 0.0280 | spots |
| Steel St3 | 10 | in electrolyte | 0.0155 | spots |
| Steel St3 | 11 | in electrolyte | 0.0102 | spots |
| Steel St3 | 13 | in electrolyte | 0.0085 | spots |
| Steel St3 | 8 | waterline zone | 0.1047 | nonuniform |
| Steel St3 | 10 | waterline zone | 0.0658 | nonuniform |
| Steel St3 | 11 | waterline zone | 0.0563 | nonuniform |
| Steel St3 | 13 | waterline zone | 0.0172 | spots |
| Cast iron SCh 18–36 | 8 | in electrolyte | 0.0426 | spots |
| Cast iron SCh 18–36 | 10 | in electrolyte | 0.0245 | spots |
| Cast iron SCh 18–36 | 11 | in electrolyte | 0.0178 | spots |
| Cast iron SCh 18–36 | 13 | in electrolyte | 0.0172 | spots |
| Cast iron SCh 18–36 | 8 | waterline zone | 0.1546 | nonuniform |
| Cast iron SCh 18–36 | 10 | waterline zone | 0.1134 | spots |
| Cast iron SCh 18–36 | 11 | waterline zone | 0.0963 | spots |
| Cast iron SCh 18–36 | 13 | waterline zone | 0.0226 | spots |

The results obtained by gravimetric measurements were supplemented with electrochemical studies of electrodes made of SCh 18–36 grade cast iron (Fig. 1).

Similar polarization curves were also obtained with St3 grade carbon steel.

The main characteristics of the anodic processes for SCh 18–36 grade cast iron depending on the pH in recycled water containing 0.02 M NaCl are summarized in Table 2.

Analysis of the data given in Table 2 shows that the effective impact of pH on the characteristics of the anode processes under the test conditions occurs at pH≥11.4. At these pH values, the stationary metal potential ennobles which is an evidence of inhibition of exactly anodic process. At pH≥11.4, the pitting potential significantly shifts to the positive side: the pit healing process proceeds faster than pit formation. This spreads the region of the passive state in the anodic polarization curve, and this region becomes equal to 1.2 V at pH=12.7.
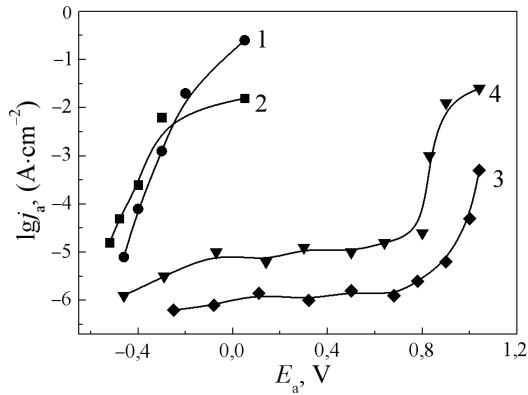
Fig. 1. Effect of solution pH on anodic polarization curves of SCh 18—36 grey cast iron in recycled water containing 0.02 M NaCl for mineralized water pH values: 7 (1); 10 (2); 11.4 (3); 12.7 (4)

Table 2

Effect of pH on the main electrochemical characteristics of anode processes occurring on SCh 18—36 grade cast iron

| pH | $E_{st}$, V | $E_{pit}$, V | ΔE, V |
|------|-------|-------|-----|
| 7.0 | −0.45 | −0.45 | N/A |
| 8.5 | −0.42 | −0.42 | N/A |
| 9.2 | −0.42 | −0.42 | N/A |
| 10.0 | −0.46 | −0.36 | 0.1 |
| 11.4 | −0.35 | +0.80 | 1.0 |
| 12.7 | −0.15 | +0.85 | 1.2 |

Thus, the shift of solution pH to the alkaline region enables an effective inhibition of ferrous metal corrosion rate in recycled water, especially in the waterline zone.

For production purposes, it is necessary to determine protection effectiveness provided by sodium hydroxide in recycled water containing 0.1 M NaCl. Addition of NaOH to water to get pH=11−13 reduces corrosion rate for the metals under study. The corrosion rate in the volume of solution decreases 3−4 times in comparison with the corrosion rate at neutral pH values (Fig. 2, curves 1 and 2). For metals in the waterline zone, the corrosion rate decreases by an order of magnitude (Fig. 2, curves 3 and 4).
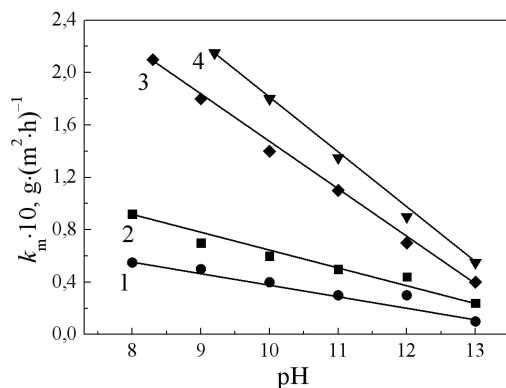


Fig. 2. Effect of pH on corrosion rate for St3 grade carbon steel and SCh 18—38 grey cast iron in recycled water containing 0.1 M NaCl: 1 — St3 in the volume of electrolyte; 2 — SCh 18—36 in the volume of electrolyte; 3 — St3 in the waterline zone; 4 — SCh 18—36 in the waterline zone

In recycled water containing 0.1 and 0.2 M NaCl, the corrosion rate for carbon steel and cast iron at pH=12 remains lower than in recycled water with NaCl concentration of 0.2 M and pH=6−8. The obtained values of corrosion rate practically do not exceed corrosion rate of these alloys in distilled water: $k_m$=0.0118−0.0176 g·(m²·h)$^{-1}$ for cast iron; and $k_m$=0.0122−0.0727 g·(m²·h)$^{-1}$ for carbon steel.

The degree of corrosion protection Z of ferrous metals with sodium hydroxide in 0.1 M NaCl solution was calculated (Table 3). Analysis of these data shows that the effective inhibitory effect of NaOH in sodium chloride solutions is manifested at pH=11.2 and sharply increases at pH=13 (Z=90 %).

The observed dependences of pH effect on the rate of corrosion of ferrous metals are explained by the nature of the change in the controlling stage. In the volume of solution, diffusion of oxygen to the metal surface is the most delayed stage of the corrosion process. With increase in pH from 7 to 12, oxygen solubility in 0.1 M NaCl solution decreases from 13.4 to 9.38 mg·l$^{-1}$. Such a change has a certain inhibitory effect on the cathodic process and the rate of corrosion on the whole. However, in general, the corrosion rate decreases due to formation of oxide-hydroxide films at alkaline pH values. The films slow down both cathode process (due to the difficulty of oxygen passage through them) and anode process. The degree of anodic control with pH growth from 7 to 12 in 0.1 M NaCl solution increases from 0 to 32.5 % for the studied metals (Table 3).

Table 3

Effect of pH on the degree of protection of St3 carbon steel and SCh 18—36 grey cast iron in 0.1 M NaCl solution

| Metal | pH | Protection degree Z, % | |
|-------|----|------|------|
| | | in electrolyte volume | in waterline zone |
| SCh 18–36 | 9 | 18.4 | 13.9 |
| SCh 18–36 | 10 | 36.7 | 28.6 |
| SCh 18–36 | 11 | 53.8 | 48.9 |
| SCh 18–36 | 12 | 71.6 | 57.8 |
| SCh 18–36 | 13 | 84.5 | 70.6 |
| St3 | 9 | 17.4 | 18.5 |
| St 3 | 10 | 34.5 | 35.6 |
| St 3 | 11 | 51.7 | 57.1 |
| St 3 | 12 | 69.1 | 72.1 |
| St 3 | 13 | 89.6 | 89.3 |

In the waterline zone where oxygen access is free, corrosion rate is determined by the anodic process of metal dissolution. Increase in pH to 11−13 promotes formation of protective films on the metal. The films directly inhibit the diffusion process, so the inhibiting effect of NaOH in the waterline zone is higher than in the volume of electrolyte.

The obtained dependences were confirmed by the results of electrochemical studies. Fig. 3 shows cathodic and anodic polarization dependences obtained in recycled water with concentration of 0.1 M NaCl and pH=12. When the cathodic potential is imposed, positive current is first observed indicating that the surfaces of cast iron and carbon steel are depassivated by cathodic polarization. The cathodic polarization curve plotted from stationary potential passes at higher current densities and more positive potentials. This confirms the possibility of reduction of the oxide film along with the basic cathodic process. The slope of the polarization curve at current densities of 10$^{-6}$ to 10$^{-5}$ A·cm$^{-2}$ was of the order of 0.1 V.

At higher current densities, a more drastic potential shift to the negative side was observed. The current densities at a reverse course of the cathode curve on the reduced surface were approximately 5 times smaller than the direct course currents.
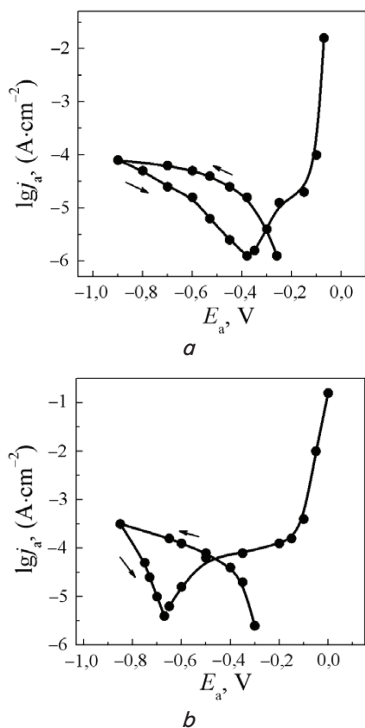


Fig. 3. Polarization dependences of ferrous metals in mineralized circulating water: $a$ — cathode and anode dependences on SCh 18—36 grey cast iron; $b$ — cathode and anode dependences on St3 carbon steel; $c(NaCl) = 0.1$ M; pH = 12

There is a section of passive state in the anode curve equal to 0.2 V for cast iron and 0.35 V for carbon steel. The pitting process begins at a potential of −0.1 V on cast iron and at a potential of +0.15 V on carbon steel. The stationary potentials of cast iron (−0.25 V) and carbon steel (−0.2 V) fall into the region of passive state. Thus, at pH = 12 in a 0.1 M NaCl solution, cast iron and carbon steel corrode from a passive state in which anodic process is the determining stage.

The effect of pH on the anodic polarization curves was studied for both metals in NaCl solution at a concentration of 0.1 M (Fig. 4, $a$). For cast iron, the effect of pH in water with a concentration of 0.2 M NaCl was additionally studied (Fig. 4, $b$). The experimental data presented in Fig. 3 show that cast iron and carbon steel have an extensive passive state region at pH > 10. At pH = 10, the region of the passive state is insignificant, and at pH < 10 this region is absent in the anode curve. A similar regularity was obtained for cast iron in a 0.2 M NaCl solution.

The main characteristics of the anode processes taking place on cast iron and carbon steel depending on mineralized water pH are given in Table 4. At the studied NaCl concentrations, a significant region of passive state appears on the anodic polarization curve at pH ≥ 11.4. At pH < 10, there is no passive state on cast iron. Carbon steel shows a slightly higher tendency to the passive state. In this curve, the slowness of the anodic process is observed at pH ≥ 9.2. It is the slowness of the anode process due to the passive state of the metal that leads to a decrease in the metal corrosion rate.
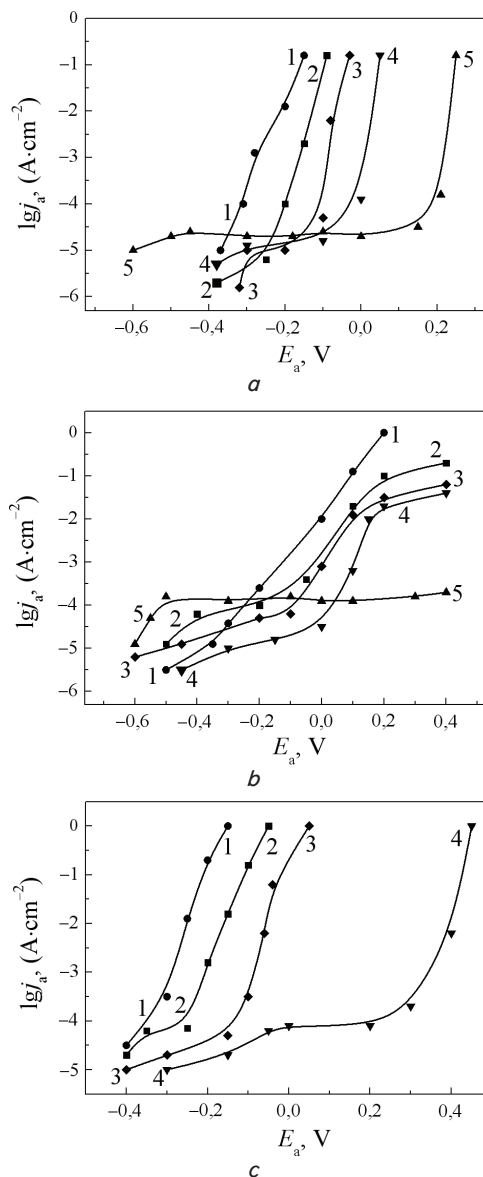


Fig. 4. Effect of pH on polarization dependencies: $a$ — polarization dependencies of SCh 18—36 grey cast iron in recycled water containing 0.1 M NaCl, solution pH: 8.1 (1); 9.2 (2); 11 (3); 11.4 (4); 12.7 (5); $b$ — polarization dependences of St3 carbon steel in recycled water containing 0.1 M NaCl, solution pH: 8.1 (1); 9.2 (2); 11 (3); 11.4 (4); 12.7 (5); $c$ — polarization dependencies of 18—36 grey cast iron in recycled water containing 0.2 M NaCl, solution pH: 8.5 (1); 10 (2); 11.4 (3); 12.7 (4)

Thus, a reliable protective effect of NaOH in recycled water with 0.1 M NaCl was observed for carbon steel and grey cast iron at pH ≥ 11.4 (Table 4).

The data given in Table 4 indicate that an increase in the pH of circulating water causes transfer of cast iron and steel into a passive state. With increase in pH, $E_{pit}$ of the studied samples is shifted to the range of positive values. This indicates the fact that the speed of the process stopping growth of pitting starts to exceed the rate of its formation, which is the proof of inhibition of the anodic reaction. The tendency of passage into a passive state is especially noticeable for gray cast iron. For this alloy, it increases with increase in water pH and decreases with the growth of water mineralization.

Table 4

Effect of pH on electrochemical characteristics of anode processes taking place on cast iron and carbon steel

| Metal | c(NaCl), M | pH | $E_{st}$, V | $E_{pit}$, V | ΔE, V |
|---|---|---|---|---|---|
| SCh 18–36 | 0.02 | 7.0 | −0.45 | −0.45 | N/A |
| SCh 18–36 | 0.02 | 8.5 | −0.42 | −0.42 | N/A |
| SCh 18–36 | 0.02 | 9.2 | −0.42 | −0.42 | N/A |
| SCh 18–36 | 0.02 | 10.0 | −0.46 | −0.46 | N/A |
| SCh 18–36 | 0.02 | 11.4 | −0.35 | +0.80 | 1.20 |
| SCh 18–36 | 0.02 | 12.7 | −0.15 | +0.85 | 1.00 |
| SCh 18–36 | 0.1 | 7.0 | −0,35 | −0.35 | N/A |
| SCh 18–36 | 0.1 | 8.5 | −0.35 | −0.35 | N/A |
| SCh 18–36 | 0.1 | 9.2 | −0.30 | −0.30 | N/A |
| SCh 18–36 | 0.1 | 10.0 | −0.35 | −0.28 | 0.07 |
| SCh 18–36 | 0.1 | 11.4 | −0.35 | −0.15 | 0.20 |
| SCh 18–36 | 0.1 | 12.7 | −0.25 | +0.20 | 0.70 |
| SCh 18–36 | 0.2 | 7.0 | −0.25 | −0.25 | N/A |
| SCh 18–36 | 0.2 | 8.5 | −0.30 | −0.30 | N/A |
| SCh 18–36 | 0.2 | 9.2 | −0.40 | −0.40 | N/A |
| SCh 18–36 | 0.2 | 10.0 | −0.30 | −0.25 | 0.05 |
| SCh 18–36 | 0.2 | 11.4 | −0,30 | −0.10 | 0.20 |
| SCh 18–36 | 0,2 | 12.7 | −0,30 | −0.10 | 0.55 |
| St 3 | 0.1 | 7.0 | −0,35 | −0.35 | N/A |
| St 3 | 0.1 | 8.5 | −035 | −0.35 | N/A |
| St 3 | 0.1 | 9.2 | −0.30 | −0.05 | 0.25 |
| St 3 | 0.1 | 10.0 | – | – | – |
| St 3 | 0.1 | 11.4 | −0.30 | +0.1 | 0.40 |
| St3 | 0.1 | 12.7 | −0.30 | – | – |

## 6. Discussion of the results obtained in corrosion studies of grey cast iron and steel in circulating water

Inhibition of the rate of steel and cast iron corrosion with NaOH is due to the metal transfer into a passive state in which it can manifest its tendency to pitting corrosion. Such property of these alloys has been studied by the method of cyclic polarization. In the anodic sections of the dependencies plotted for the metal in a solution with pH=12, an extensive region of the passive state is observed. In media with pH=10, this region is insignificant, and it is absent at pH 8. An increase in the region of passive state with increase in pH is associated with the shift of the pitting potential $E_{pit}$ to the positive side while the value of the stationary potential $E_{st}$ does not change much. The repassivation potential $E_{rp}$ shifts in a positive direction with an increase in pH which is explained by the growth of the tendency to self-healing the formed pits.

The difference between the pitting potential $E_{pp}$ and $E_{rp}$ increases with increase in pH and reaches +0.75 V at pH=12. This is connected with a more significant shift of $E_{pp}$ in the positive direction compared to $E_{rp}$. Different growth rates of $E_{pp}$ and $E_{rp}$ with increase in pH show that the process of stopping growth of pits is much more difficult than their formation. At pH=12, the region of passive state in the anode curve is retained, and when its course is repeated, it amounts to 0.1 V. When the curves are re-swept in the range of pH 8–12, the $E_{pp}$ is shifted to the cathode region by 0.02–0.25 V as compared to $E_{pp}$ on the initial electrode surface. In solutions with pH=13, such a shift is not observed. This is explained by the fact that the pits formed at pH≤12 are healed slowly thereby reducing $E_{pp}$ in the repeated course of the curve.

With an increase in pH, the anode current densities decrease which is explained by the inhibitory effect of NaOH.

The obtained dependences show an increase in the cathode current in the potential region (−0.7)–(−0.8) V. When the course is repeated, this effect becomes more pronounced. The increase in the cathode current in this region of potentials according to the Purbe diagram can be explained by the process of reduction of iron oxides or hydroxides by the following reactions:

$$Fe_3O_4+8H^++8e \rightarrow 3Fe+4H_2O;$$

$$E_p=(-0,085)-0,059pH; \tag{1}$$

$$Fe(OH)_2+2H^++2e \rightarrow 3Fe+2H_2O;$$
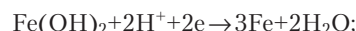
$$E_p=(-0,047)-0,059pH. \tag{2}$$

This is confirmed by the fact that $E_{st}$ grows to −0.68 V after cycling at pH 8. When reactions (1), (2) proceed, reduced iron with an active, non-oxidized surface forms on the electrode surface. This causes the potential shift in the negative direction.

With increase in pH, the current grows due to reaction (2) which can be explained by strengthening of $Fe(OH)_2$ adhesion to the metal.

Based on the dependences obtained, main electrochemical characteristics of steel in 0.1 M NaCl solution were determined (Table 5).

Table 5

Effect of pH on the main electrochemical characteristics of steel in a 0.1 M NaCl solution

| pH | $E_{st}$, V | $E_{pp}$ of initial surface, V | ΔE, V | $E_{rp}$, V | $E_{pp}-E_{rp}$, V | $E_{pp}$, V | E of metal after experiment, V |
|---|---|---|---|---|---|---|---|
| 8 | −0.35 | −0.35 | 0.0 | −0.38 | 0.08 | −0.32 | −0.68 |
| 10 | −0.32 | −0.15 | 0.15 | −0.32 | 0.17 | −0.30 | −0.52 |
| 12 | −0.30 | +0.52 | 0.82 | −0.25 | 0.75 | +0.75 | −0.34 |
| 13 | −0.30 | – | 0.85 | – | – | – | −0.30 |

After plotting curves in a solution with pH=12–13, potential $E_{st}$ shifts insignificantly with respect to its value on the initial surface. After cycling, the metal potential ennobles with growth of pH. These facts confirm reliability of the protective film at pH=12, even in a 0.1 M NaCl solution. The protective properties of the film improve with increase in pH. At pH=13, the anode reverse course currents are 2–3 orders of magnitude smaller than at pH=12. It can be assumed that in a solution with pH=13, the film of $Fe(OH)_2$ and γ-$Fe_2O_3$ formed during oxidation is so strong that that it retains even when the curve course is reversed. It is obvious that a sharp increase in the anode current at pH=13 is due to the process of oxygen evolution from water at E>0.6 V by the following reaction:

$$2H_2O-4e \rightarrow O_2+4H^+; \tag{3}$$

$$E_p=1,218-0,059pH \text{ (at } p(O_2)=21,21 \text{ kPa).} \tag{4}$$

The calculated value of potential was −0.46 V when pH=13 was substituted into equation (4) which was close to the experimental value.

Reduction of iron corrosion rate in alkaline solutions is traditionally associated with the protective action of the

oxides being formed. It is believed that hydroxide films do not possess protective properties. This is due to the looseness and porosity of hydroxide films causing their weak bond with the metal surface. Formation of a protective layer is explained by the following scheme: during anodic polarization, $Fe^{2+}$ ions migrate into solution and immediately react with hydroxyl ions with formation of $Fe(OH)_2$ precipitate. The precipitate contacting with the metal undergoes further anodic oxidation and a dense oxide layer is formed which prevents further metal dissolution. Thus, the following scheme of protective oxide formation is proposed [14]:

$$Fe \rightarrow Fe^{2+} \rightarrow Fe(OH)_2 \rightarrow Fe_2O_3. \qquad (5)$$

Possibly, the main cause of decrease in iron corrosion rate in alkaline media is the reduction of $Fe(OH)_2$ solubility with the growth of pH [14, 16]. The curve of dependence of iron dissolution on the solution pH obeys the same law as the curve of $Fe(OH)_2$ solubility in a NaOH solution. This correlation enables drawing a conclusion that the corrosion rate in alkaline solutions is inhibited due to a decrease in solubility of iron hydroxide.

### 7. Conclusions

1. The effect of sodium hydroxide content on the rate and nature of St3 carbon steel and SCh 18–36 grey cast iron corrosion in highly mineralized recycled water was investigated. It has been shown that an increase in water pH up to 13 caused decrease (5 to 8 times) in the rate of corrosion of the tested alloys, especially in the waterline zone. As the medium pH rose from 8 to 13, St3steel $k_m$ in the electrolyte volume dropped from 0.0280 to 0.0085 $g \cdot (m^2 \cdot h)^{-1}$. In the waterline zone, $k_m$ decreased from 0.1047 to 0.0172 $g \cdot (m^2 \cdot h)^{-1}$. The weight corrosion index for SCh 18–36 cast iron varied from 0.0426 to 0.0172 and from 0.1546 to 0.0226 $g \cdot (m^2 \cdot h)^{-1}$ respectively. The values obtained did not exceed the rate of corrosion of these alloys in distilled water and were in the range of acceptable values.

2. Based on electrochemical studies, it has been established that the inhibiting effect of NaOH on the anodic process was most effective at values of pH≥11.4 for cast iron. This fact was confirmed by ennobling of the metal stationary potential which was the indication of the anode process inhibition. At pH≥11.4, the pitting potential significantly shifted to the positive side and the process of healing pits was faster than their formation. The passive state region in the anode polarization dependences increased from 0.1 V at pH=10 to 1.2 V at pH=12.7. The effect of pH on the anodic polarization dependences of St3 steel in a 0.1 M solution of NaCl and SCh 18–36 cast iron in a 0.02, 0.1 and 0.2 M NaCl was studied. It has been established that steel and especially cast iron tend to pass into a passive state at pH>10. The passive state region of the alloys is insignificant at pH=10 and it is absent at pH<10. The effect of pH on the tendency of steel and cast iron to passivation and pitting corrosion in recycled water containing 0.1 M NaCl was studied by cyclic polarization. It was shown that there was an increase in the passive state region and the repassivation potential magnitude as well as a decrease in anode currents with pH rise.

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*Запропоновано технічні рішення, які дозволяють отримувати якісне дизельне біопаливо за рахунок забезпечення перемішування шарів емульсії із використанням циркуляційних змішувачів-розділювачів. Встановлено параметри установки для виробництва дизельного біопалива. Запропоновано використання дизельного біопалива в тракторних двигунах із двоступеневої системою підігріву. Застосування змішувачів дозволяє отримувати дизельне біопаливо за спрощеною технологією в агровиробництві. Застосування системи підігріву розширює температурний діапазон використання чистого дизельного біопалива та зменшує його витрату*

*Ключові слова: дизельне біопаливо, переетерифікація, змішувач, машинно-тракторний агрегат, система підігріву*

*Предложены технические решения, которые позволяют получать качественное дизельное биотопливо за счет обеспечения перемешивания слоев эмульсии с использованием циркуляционных смесителей-разделителей. Установлены параметры установки для производства дизельного биотоплива. Предложено использование дизельного биотоплива в тракторных двигателях с двухступенчатой системой подогрева. Применение смесителей позволяет получать дизельное биотопливо по упрощенной технологии в агропроизводстве. Применение системы подогрева расширяет температурный диапазон использования чистого дизельного биотоплива и уменьшает его расход*

*Ключевые слова: дизельное биотопливо, переэтерификация, смеситель, машинно-тракторный агрегат, система подогрева*

# RATIONALE FOR THE PARAMETERS OF EQUIPMENT FOR PRODUCTION AND USE OF BIODIESEL IN AGRICULTURAL PRODUCTION

**G. Golub**
Doctor of Technical Sciences, Professor, Head of Department*
E-mail: gagolub@mail.ru

**S. Kukharets**
Doctor of Technical Sciences,
Associate Professor, Head of Department
Department of mechanical engineering and agroecosystems***
E-mail: saveliy_76@ukr.net

**V. Chuba**
PhD, Associate Professor
Department of transport technologies and means in AIC**
E-mail: vvchuba@ukr.net

**M. Pavlenko**
PhD, Senior Lecturer*
E-mail: maxim_pavlenko@i.ua

**Y. Yarosh**
PhD, Associate Professor***
E-mail: yaroslav.yarosh76@gmail.com
*Department of tractors, cars and bioenergosistem**
**National University of Life and
environmental sciences of Ukraine
Heroyiv Oborony str., 15, Kyiv, Ukraine, 03041
***Zhytomyr National Agroecological University
Staryi blvd., 7, Zhytomyr, Ukraine, 10008

## 1. Introduction

One of the factors increasing the energy efficiency of agricultural production and reducing carbon dioxide emissions is the use of fuel of own production, in particular, liquid biodiesel [1, 2].

For biodiesel production, transesterification process is used [3]. For rapid and complete reaction, methanol and alkaline catalyst are used in the process of transesterification [4–6]. After the transesterification reaction, separation of a glycerol phase and a phase containing fatty acid methyl esters occurs. After adding a methanol-catalyst solution in oil,