

Shuryberko Mariia

Postgraduate student

Department of Ecology and Technology of Plant Polymers,
Igor Sikorsky Kyiv Polytechnic Institute**Shabliy Tetyana**

Doctor of Technical Sciences, Professor

Department of Ecology and Technology of Plant Polymers,
Igor Sikorsky Kyiv Polytechnic Institute**Gomelya Mykola**

Doctor of Technical Sciences, Professor, Head of Department,

Department of Ecology and Technology of Plant Polymers,
Igor Sikorsky Kyiv Polytechnic Institute**Gluchenko Nikolai**Department of operations management units with military communications facilities,
National Academy of National Guard of Ukraine**THE DEOXYGENATION OF WATER BY BATCH ON THE IRON CONTAINING COMPOSITES BASIS**

Abstract. The study on the evaluation of new iron-containing composites efficiency has been carried out in case of the deoxygenation of tap water and sodium cationized water. The efficiency of one stage deoxygenation of water is determined. The use of two-stage stabilization of water treatment, which involves the deoxygenation of water and its subsequent sodium cationite, is stipulated. The efficiency of using softened water in the removal of dissolved oxygen and iron ions has been determined. The dependence of the efficiency in the processes of the deoxygenation and iron removal of water on the filtering speed through the redox filter has been determined.

Key words: deoxygenation of water, iron-containing composites, redox filter, sodium cationite, removal of iron compounds.

Introduction. Huge volumes of water are used exactly in power engineering and cooling systems in industries. Perspective methods for ensuring economic benefits and environmental friendliness of using natural water are methods for conditioning water and applying water-circulation systems (closed and reversible). Therefore, these methods need to be continuously improved and studied in all aspects of the processes that occur in them.

The main issue in using water-recirculation systems is the need to reduce the corrosion activity and water hardness to prevent formation of scale and metal corrosion [3, 14 – 20; 11, 1 – 14]. In case of neglecting the quality requirements of water, additional expenses for the equipment repair and fresh water intake as well as discharging of purge water are increased [1, 50 – 55; 2, 6 – 10].

Therefore, it is recommended to use stable water in circulating and closed systems of cooling and heat supply. The reduction of corrosive aggressiveness of water can be achieved in different ways: the use of inhibitors of metals corrosion [4, 92 – 96; 12, 28 – 31] or the preliminary removal of aggressive gases from water – water degassing [10, 445 – 452]. Such methods are divided into chemical, physical, biochemical, physical and chemical.

The essence of chemical degassing lies in the fact that the dissolved oxygen is bound by the addition into the water of such chemicals as sulfur dioxide (SO₂), sulphuric acid (Na₂SO₃) or hydrazine (N₂H₄). Na₂SO₃ oxidizes by oxygen to sulphate in accordance with the reaction equation:



Sulphur dioxide (sulphurous acid) oxidizes to sulphuric acid by oxygen which is dissolved in water:



In practice, hydrazine can almost completely deoxygenate water [8, 132 – 139], which occurs with the emission of inert nitrogen:



This method is the most effective. The lack is the high cost of hydrazine, which leads to significant economic expenses. Therefore, this method is used, basically, for the final deoxygenation of water after physical methods.

Water treatment method such gases as nitrogen (N_2) and carbon dioxide (CO_2) using rotor-stator reactor can be used for deoxygenation. [16, 13 – 17]

One of the methods of the deoxygenation of water is the use of redoxites – cationites or anionites which is modified by reducing agents. This method completely removes ions of oxygen from water without secondary pollution. The peculiarity of redoxites is a wide variation of reduction-oxidation potential due polymeric carrier and ionic groups, high redox capacity which is provided with a great amount of functional groups, developed inside reaction surface of pores and fixation of redox-groups with a polymer chain [5, 27 – 31; 14, 58 – 62 ; 6, 1104 – 1110].

The process of the deoxygenation of water [5, 27 – 31] was carried out with an anionite in a sulphite form. The authors used desalted water and condensate. But more important and interesting is the problem of removing oxygen from water which contains the hardness ions. In this case, the process, above all, will depend on the concentration of anions. This using the reduction-oxidation potential of ion exchange resin of this type may be problematic for the cooling systems, where natural water is used without partial softening. This process was investigated by the authors [13, 91 – 94] using AV-17-8 anionite in Cl^- – and SO_4^{2-} – forms with the use of running tap water.

The authors [15] studied the effectiveness of mixture of ion exchange resins which contained cationic resin in Na^+ – form, and anionic resin in Cl^- – form. This mixture was treated with the ferrous sulphate solution (II) with sodium thiosulphate and alkali for the transformation of the metal into the insoluble state. The authors reached the reduction of solubility of the iron compounds, fixed on the surface and in pores of the filtering material. This resin treatment method provides possibility to prevent washing out iron ions from the filtering material during simultaneous sorption of oxygen dissolved in water to the concentration less than 50 mcg/dm^3 .

The author [9] offered a new chemical technology of chemical deoxygenation by the monosolution of Na_2SO_3 (10 – 15%) in a stoichiometric quantity and with a further filtration through the redox catalytic

filter. Industrial tests have shown the high efficiency of this technology.

All these methods involve the regeneration of waste redoxites.

We suggest using modified batch which contains iron composites (IC redoxite) as a reducing agent. This material is available. It is obtained from industrial waste.

The object of our research was the processes of the deoxygenation of water for ecologically safe heat supply systems and steam and electricity generation systems.

The purpose of the study was to determine the efficiency of the deoxygenation by redoxites on the basis of iron-containing composites with a reliable regulation of the iron compounds content in deoxygenated water.

The following tasks were solved to achieve this goal:

- the efficiency estimation of new iron-containing composites at the deoxygenation of tap water and sodium-cationized water;
- the determination of conditions for the removal of iron compounds from deoxygenated tap water and softened water;
- the determination of the efficiency dependence for the processes of the removal of iron compounds and the deoxygenation of water on the rate of filtering through the redox filter.

Materials and methods. In this paper the processes of oxygen remove from water were studied by filtration successively through a column filled with the iron-containing composite and a column filled with KU-2-8 cationite in Na^+ -form ($V_i = 50 \text{ cm}^3$). The installation diagram is shown in Fig. 1. Tap water (TH = $4,6 \text{ mg-equiv/dm}^3$; A = $4,5 \text{ mg-equiv/dm}^3$; $[Ca^{2+}] = 3,8 \text{ mg-equiv/dm}^3$; pH = 7,500; $[Cl^-] = 37,5 \text{ mg/dm}^3$; $[SO_4^{2-}] = 23,0 \text{ mg/dm}^3$) and sodium cationized water (TH = $0,0 \text{ mg-equiv/dm}^3$; A = $4,8 \text{ mg-equiv/dm}^3$; pH = 7,851) was filtered at a rate of 2,12 – 10,60 m/h. Water was taken after a column filled with redoxite in the first experiments. All water quality indicators were determined according to the methods described in [7]. In subsequent experiments water was collected after the successive filtration through the redoxite and cationite column. In the samples taken the residual concentrations of oxygen, iron and pH of the medium were determined. The residual water hardness was determined in the case of filtering tap water through a sorbent and cationite.

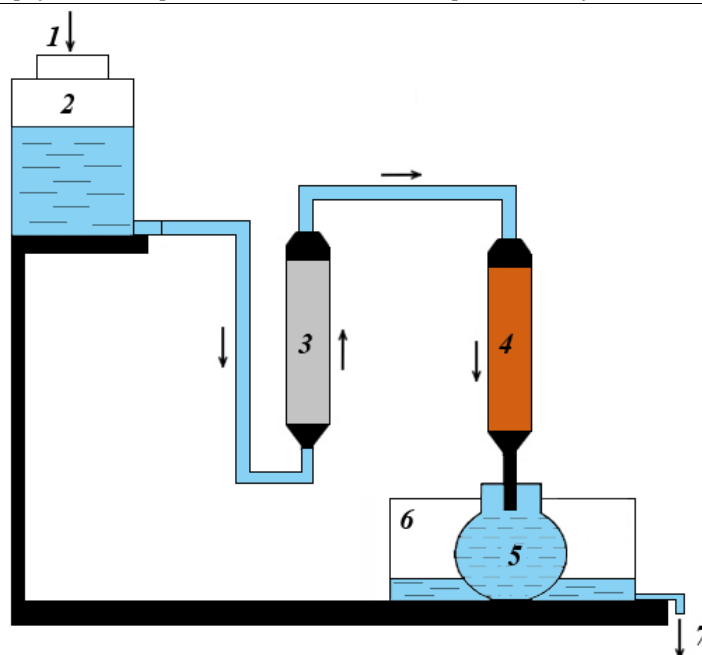


Fig. 1. Experimental installation for the deoxygenation of water: 1 – water supply; 2 – water tank; 3 – column with IC redoxite; 4 – cationite in Na⁺-form; 5 – Winkler flask; 6 – tank for collecting displaced water from a flask; 7 – removal of excess water into the sewage system

Results and discussion. At the first stage of the research the tap water of Kyiv was used, which was passed through a column batch which contains iron composites (IC redoxite) as a reducing agent. During the studies the oxygen content was measured before

and after the experiment, the total iron content, the total water hardness and pH. The results of the deoxygenation of tap water with IC redoxite are shown in Figure 2:

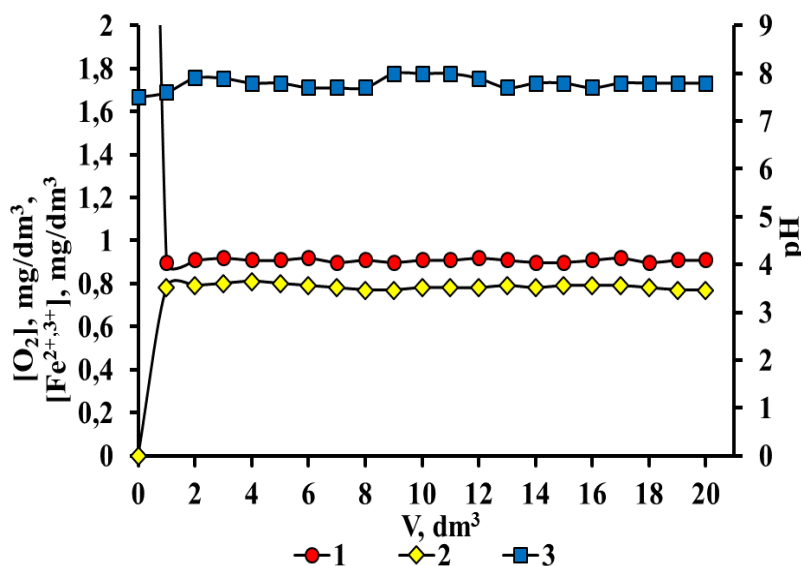


Fig. 2. The dependence of the dissolved oxygen concentration (1), concentration of iron ions (2) and pH (3) on the volume of tap water which was passed through the IC redoxite (pH = 7,500; [O₂] = 8,05 mg/dm³; TH = 4,6 mg-equiv/dm³). The filtering speed is 2,12 m/h

As it can be seen from the picture below, when water passes through the IC redoxite, there is an oxygen

reduction due to the interaction with the iron compounds:



As a result of the contact of metal and oxygen dissolved in water the oxygen concentration is reduced by approximately 8,5 times (from 8,05 to 0,91 mgO₂/dm³). This method allows to reduce the concentration of oxygen in water, but is accompanied by an increase in the concentration of iron ions which average content is equal to 0,78 mg/dm³, and the water hardness remains at the initial level (TH = 4,6 mg-equiv/dm³).

In order to prevent the secondary contamination by iron ions water after the filtration through the IC redoxite (process of deoxygenation) was passed through the strongly acidic KU-2-8 cationite in the Na⁺-form. The oxygen content, concentration of iron ions, pH and the total hardness were determined in selected samples of water (V = 1 dm³). The results of the deoxygenation of tap water during successive treatment with the IC redoxite and KU-2-8 cationite in the Na⁺-form are shown in Figure 3.

During applying a two-stage stabilization system there is a decrease in the concentration of dissolved

oxygen from 8,05 to 0,59 mgO₂/dm³. The removal of secondary pollutant (iron) from water is provided due the ion exchange on the cationite. In this case the concentration of iron decreases from 0,78 to 0,1 mg/dm³. In addition, as a result of a two-stage treatment the hardness of water decreases to zero with its subsequent increase in the values due to the exhaustion of the ion exchanger capacity.

It should be noted that the increase in the efficiency of oxygen removal occurs due to its binding in interaction with iron cations (II), which sorbed on cationites.

The efficiency of cationite in absorbing iron ions decreases as it saturates with calcium ions. Therefore, the concentration of iron ions in the solution increases due the exhaustion of ionite capacity by the ions of Ca²⁺. At the same time the pH decreases to a certain extent (Fig. 4), which also leads to a decrease in the efficiency of binding oxygen with sorbed iron ions.

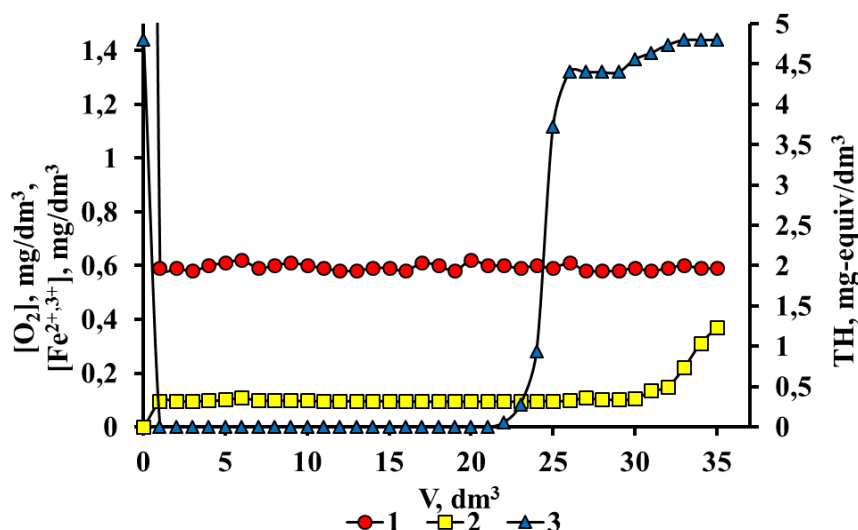


Fig. 3. The dependence of the concentration of dissolved oxygen (1), concentration of iron ions (2) and water hardness (TH) (3) on the volume of tap water which was passed through the IC redoxite and KU-2-8 cationite in Na⁺-form (pH = 7,786; [O₂] = 9,23 mg/dm³; TH = 4,8 mg-equiv/dm³). The filtering speed is 2,12 m/h

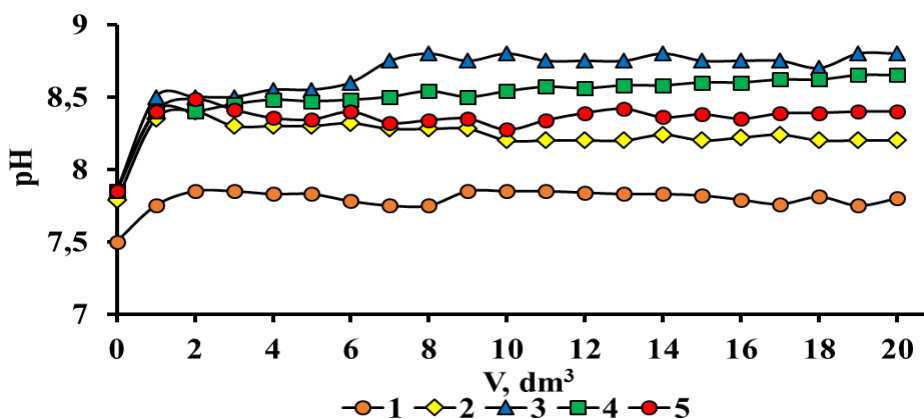


Fig. 4. The dependence of pH on the volume of tap water (1, 2) and Na⁺-cationized water (3; 4; 5) which was passed through IC redoxite (1) and KU-2-8 cationite in Na⁺-form (2; 3; 4; 5) at different filtration rates, m/h: 2,12 (1; 2; 3); 6,36 (4); 10,6 (5)

After the regeneration of cationite with a solution of sodium chloride, its activity increases and it provides the effective removal of iron at the level shown in Fig. 3

Normally, softened (sodium-cationic) or desalted water is used in water supply systems and during water supply to water heaters and steam boilers. In this case, sodium-cationized water was used, for which a three-stage water treatment was performed: water softening

by KU-2-8 cationite in Na⁺-form, the deoxygenation of water by IC redoxite and removal of iron ions by KU-2-8 cationite in Na⁺-form. The oxygen content in water, concentration of iron ions and pH were determined in selected samples of water ($V = 1 \text{ dm}^3$). The results of the deoxygenation of Na⁺-cationized water due the IC redoxite with subsequent passage through KU-2-8 cationite in the Na⁺-form are shown in Figure 5.

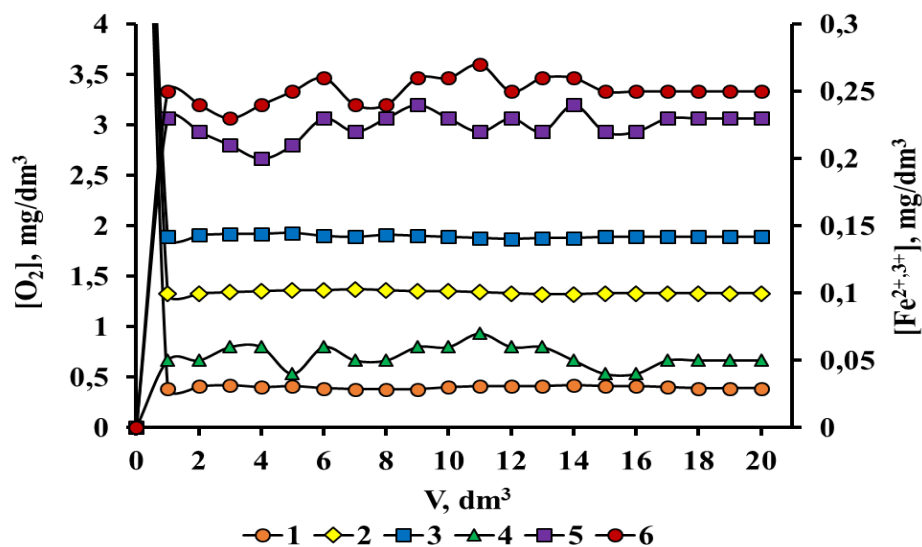


Fig. 5. The dependence of the concentration of dissolved oxygen (1; 2; 3) and concentration of iron ions (4; 5; 6) on the volume of Na⁺-cationized water ($[O_2] = 9,74 \text{ mg/dm}^3$; $pH = 7,851$) which was passed through IC redoxite and KU-2-8 cationite in Na⁺-form at different filtration rates, m/h : 2,12 (1; 4); 6,36 (2; 5); 10,6 (3; 6).

From the analysis of the results presented in Figure 5, it is evident that the deoxygenation of sodium cationized water, in which the concentration of ions of hardness is at zero level, the concentration of dissolved oxygen ranges about $0,39 \text{ mgO}_2/\text{dm}^3$, the concentration of residual iron on average reaches $0,06 \text{ mg/dm}^3$.

It should be noted that the separate removal of cations, such as ions of hardness and iron ions from ion exchange resins, allows receiving separate waste regenerative solutions which can be easily processed.

Since the process of water deoxygenation occurs as a result of chemical reaction – the oxidation of iron compounds, it is advisable to carry out studies to determine the dependence of the water deoxygenation efficiency on the rate of filtration through the batch. The filtration rate varied from 2,12 to 10,6 m/h . The concentration of oxygen, concentration of iron ions and pH were determined in the samples taken. The results of the study are shown in Figures 4, 5 and 6.

As expected, the rate of filtration significantly affects the efficiency of the deoxygenation and removal of secondary pollutant – iron ions from water. These studies showed a linear back dependence of the efficiency of compounds removal on the filtration rate. The oxygen content increases by 2,5 – 3 times (increases from 0,39 to $1,39 \text{ mg/dm}^3$) if the rate of

filtration increases in 2,5 – 3 times. And the oxygen content increases by 5 times (from 0,39 to $1,89 \text{ mg/dm}^3$) with a greater increase in the rate of filtration up to 10,6 m/h . The same trend is observed for iron ions remove processes. Although the iron content is negligible, it also increases with an increase in the filtration rate from $0,06 \text{ mg/dm}^3$ at the filtering speed 2,12 m/h to $0,25 \text{ mg/dm}^3$ at the filtering speed 10,6 m/h .

In general, the use of redoxite from modified iron compounds provides a sufficiently effective removal of oxygen from water.

As it can be seen from Fig. 6, at the treatment of tap water by the IC redoxite, the degree of the deoxygenation of water was achieved at the level of 87 – 90 % at a filtering rate of 2,12 m/h at a batch volume of 50 cm^3 . The contact time of water with the sorbent is very small to ensure the complete oxygen binding at such a batch volume. However, at the time of application of the sodium cation filter, the degree of the deoxygenation of water increased to 93 – 94 % with practically complete removal of iron ions from water. And the degree of the deoxygenation of water reached 97 % when using sodium cationized water and two-stage filtration. Obviously, with the increase in the volume of redox batch, it is possible to achieve the complete deoxygenation of water.

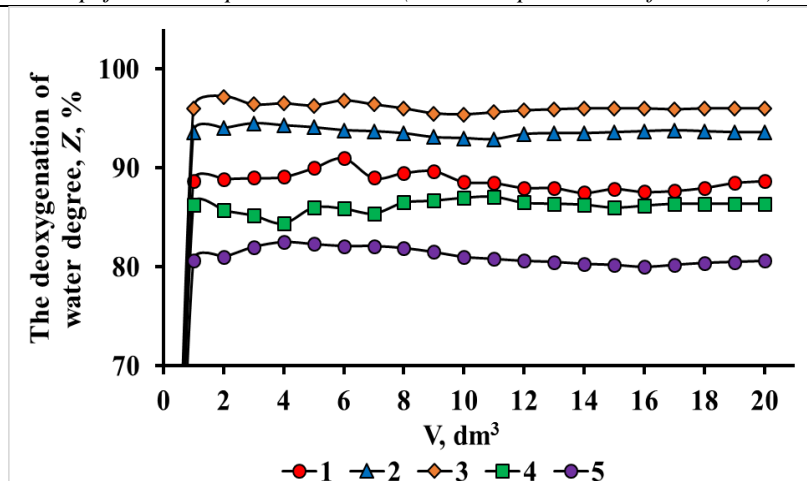


Fig. 6. The dependence of the deoxygenation of water degree (Z,%) on the volume of tap water (1; 2) and Na^+ -cationized water (3; 4; 5) which was passed through IC redoxite and KU-2-8 cationite in Na^+ -form (2; 3; 4; 5) at filtration rates, m/h: 2,12 (1; 2; 3); 6,36 (4); 10,6 (5); pH: 7,500 (1; 2); 7,851 (3; 4; 5); $[\text{O}_2]$, mg/dm³: 8,05 (1); 9,23 (2); 9,74 (3; 4; 5)

The fact that with increasing the rate of filtration, the efficiency of the deoxygenation of water is reduced, only confirms the fact that at a constant rate of interaction of redoxite with oxygen, the degree of binding decreases with a decrease in contact time with the sorbent. This parameter can be changed by increasing the volume of redox batch. Therefore, in future studies, optimal correlations will be determined between the volume of redox batch, the filter diameter and the height of the redoxite batch at the selected filtering rates.

Conclusions

1. The efficiency of one-stage deoxygenation of water by IC redoxite has been determined, and it is established that this sorbent allows to reduce the concentration of dissolved oxygen in water from 6 to 8 times from the initial value of 8 to 9 mgO₂/dm³ to 0,91 mgO₂/dm³. The process of the deoxygenation of water is accompanied by secondary pollution of water by iron ions ($[\text{Fe}] \leq 0,78 \text{ mg/dm}^3$).

2. The two-stage stabilization treatment, which involves the deoxygenation of water and its subsequent sodium cationization, is more efficient. The content of oxygen dissolved in water decreases in comparison with one-stage treatment to 0,59 mgO₂/dm³, and the secondary pollution of water by iron ions does not occur. At the same time, ions of hardness are removed. The saturate of ion exchange resins by ions Ca^{2+} , Mg^{2+} involves the reduce of efficiency of removal of iron ions.

3. The use of softened water increases the efficiency of water deoxygenation in the filter filled with redoxite and the cationite filter in Na^+ -form as well as the efficiency of removal of iron ions.

4. The influence of the filtration rate on the processes of water deoxygenation and removal of iron ions have been investigated. The linear back dependence of the removal efficiency of compounds on the filtration rate is shown. The oxygen content increases by 2,5 – 3 times if the rate of filtration increases in 2,5 – 3 times. And the oxygen content increases by 5 times with an increase in the rate of

filtration by 5 times. The same trend is observed for iron ions remove processes. This tendency is due to a decrease in the contact time of water with sorbent and ion exchange resins at constant values of the oxidation rate for iron compounds and sorption of iron ions on the cationite.

References

- Bernstein Hans - Friedrich. 2008. Water degassing in the networks of hot water supply. Euroheat and power, 37(6), 50–55.
- Cervova J., Hagarova M., Lackova P. 2014. Corrosive protection of metal materials in cooling water. American Journal of Materials Science and Application, 1, 6–10.
- Chychenin V. V., Kishnevskiy V. A., Grytsaenko A. S., Akhrameev V. G., Shulyak Y. D. (2015). Study of corrosion rate and accumulation of deposits under circulating water concentration in bench experiments. Easten-Europen journal of Enterprise Technologies, 5/8(77), 14–20.
- Gomelya N. D., Shabliy N. A., Trohymenko A. G., Shuryberko M. M. 2017. New inhibitors of corrosion and depositions of sediments for water circulation systems. Journal of Water Chemistry and Technology, 39, 92–96.
- Homelia N. D., Tamazashvili A. T. 2012. Evaluation of reducing ability of anion exchange resin av-17-8 in sulphite form. Easten-Europen journal of Enterprise Technologies, 3/6 (57), 27–31.
- Kipriyanova E.S., Kravchenko T.A., Konev D.V., Kalinichev A.I., Hoell W.H. 2010. Reductive sorption of molecular oxygen from water on silver-KU-23 sulfo-cation exchanger nanocomposites in different ionic forms. Russian Journal of Physical Chemistry A, 84 (6), 1104–1110.
- Lurier Y.Y. 1989. Directory on Analytical Chemistry. Moscow.
- Medvedev R. B., Merdukh S. L. 2013. Water-chemical regime and mathematical modeling of the Second Contour of the NPP plant with VEPP-1000 reactor. Scientific News of NTUU "KPI", 3, 132–139.

9. Porzhezinsky Y. G. 2015. New technology for chemical deoxygenation of water. Kyiv.
10. Siwiec T., Michel M. M., Reczek L., Nowak P. 2016. The influence of aeration on the change in corrosiveness and aggressiveness of groundwater. *Water Science and Technology: Water Supply*, 6, 2, 445–452.
11. Strelkov A. K., Tsabilev O. V., Vasiliev V. V., Solodyannikova Yu. V. 2013. Evaluation of the expediency of utility drinking water stabilization. *Water Supply and Sanitary Technique*, 8, 1–14.
12. Tamazashvili A.T., Mazna Y.I., Sirenko L.V. 2012. Comparison of the efficiency of phosphate inhibitors of steel corrosion in tap water. *Easten-European journal of Enterprise Technologies*, 2/13 (56), 28 – 31.
13. Tamazashvili A., Makarenko I. 2015. Evaluation of the reducing ability of anion exchange resin AV-17-8 in the sulphite form. *Chemistry & chemical technology*, 1, 91–94.
14. Tamazashvili A. T., Kamaev V.S., Homelia N. D. 2011. Evaluation of the effectiveness of the redoxite depending on the type of cation exchange resin and the method of its modification. *Energy Technologies and Resource Saving*, 6, 58–62.
15. Troyatsky M. V., Masalitin V. M., Gomelya N. D. 2010. Method of obtaining a filter material for filters intended for the deoxygenation of water: Patent 89903 Ukraine: IPC: B01J 20/20, B01J 20/30, E03B 3/00, B01D 39/16. No. u200811234; Appl. September 16, 2008; Publ. Mar 10, 2010, Bul. № 5.
16. Zhao Z., Song Y., Chen J., Chu G., Chen J, Shao L. 2017. Study of water deoxygenation using a rotor-stator reactor. *Beijing Huagong Daxue Xuebao (Ziran Kexueban) / Journal of Beijing University of Chemical Technology (Natural Science Edition)*, 44(1), 13–17.