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# ASSESSMENT OF DEOXYGENATION EFFICIENCY FOR WATER OF VARIOUS MINERALIZATION

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### Abstract

The study of the influence of iron-containing redoxites on the efficiency of water deoxidation was carried out and described. During this study, the dependence of the efficiency of water deoxygenation on the filtration speed (from 1.50 to 7.50 m/h) was also determined. The residual content of oxygen and the content of dissolved iron in water were determined. As a result, it was shown that an increase in the filtration rate within the specified limits has a rather strong effect on the residual oxygen concentration, namely its increase from 0.30 mg/dm<sup>3</sup> to 1.51 mg/dm<sup>3</sup>. The residual oxygen content also depends on the reaction of the medium, since an increase in the residual oxygen content was noted when the pH of the medium increased from 7.770 to 9.75, but the residual iron content was little dependent on these factors (in all cases it did not exceed 0.25 mg/dm<sup>3</sup>). When using columns with KU-2-8 cationite in the Na<sup>+</sup> form in the scheme of the redox system, almost complete removal of iron ions from water and sodium cation softening of tap water was noted.

Keywords: corrosion; redoxite; water deoxidation; water deironing; oxygen depolarization; sodium cationization.

### ВИЗНАЧЕННЯ ЕФЕКТИВНОСТІ ЗНЕКИСНЕННЯ ВОДИ РІЗНОЇ МІНЕРАЛІЗАЦІЇ

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### Анотація

Проведена та описана робота по дослідженню впливу на ефективність знекиснення води залізовмісних редокситів. Протягом цього дослідження також визначали залежність ефективності знекиснення води від швидкості фільтрування (від 1.50 до 7.50 м/год). Визначався залишковий вміст кисню та вміст розчиненого заліза у воді. В результаті було показано, що збільшення швидкості фільтрування у вказаних межах досить сильно впливає на залишкову концентрацію кисню, а саме викликає її зростання від 0.30 мг/дм<sup>3</sup> до 1.51 мг/дм<sup>3</sup>. Залишковий вміст кисню також залежить від реакції середовища оскільки було відмічено зростання залишкової концентрації кисню за умови підвищення pH середовища від 7.770 до 9.750, проте залишковий вміст заліза мало залежить від цих факторів (у всіх випадках не перевищував 0.25 мг/дм<sup>3</sup>). За використання у схемі установки з редокситом, а також колонки із катіонітом КУ-2-8 у Na<sup>+</sup>-формі відмічено практично повне вилучення іонів заліза із води та натрійкатіонне пом'якшення водопровідної води.

Ключові слова: корозія; редоксит; знекиснення води; знезалізнення води; киснева деполяризація; натрійкатіонування.

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## Introduction

Water resources are an essential component of industry. The large volumes of water are primarily used in energy production and cooling systems in the industry. Industrial enterprises consume significant amounts of water, and some of them require a continuous water supply. The water consumption by enterprises exceeds the amount of water consumed by the population by tens of times. The quality and quantity of water for production purposes depend on various factors, including water sources, the nature of production, the technological process, and the equipment used. These factors can vary widely.

Promising methods for ensuring economic benefits and environmental sustainability in the use of natural water resources include water conditioning methods and the application of water circulation systems (closed-loop and recirculating systems). Therefore, these methods need to be constantly improved, and all aspects of the processes involved in them should be studied. In heating, cooling, hot water and steam production, and electricity generation systems, a significant amount of attention is always given to equipment corrosion protection issues.

Removal of Dissolved Oxygen from Water is a crucial process in many industrial sectors, used to reduce corrosion, poor heat transfer, and oxidation of food products and medicines. Corrosion is a problem in steam and energy production. This type of corrosion occurs in the presence of dissolved oxygen and leads to the formation of galvanic cells in water, increasing the corrosion rate. Therefore, removing dissolved oxygen is essential for controlling this type of corrosion [1–3].

For systems with temperatures up to 40 °C and normal oxygen saturation in water, inhibitors-passivators are effective, including phosphonic acids, phosphates, pyrophosphates, and phosphinates [4]. Their effectiveness increases in the presence of zinc ions and other metals [5].

In highly mineralized water with high temperatures, inhibitors-passivators are less effective. The desired effect of reducing metal corrosion rates is achieved through water deoxygenation.

The corrosive activity of water primarily depends on its dissolved oxygen content. As a result of iron oxidation, corrosion products are formed, including iron oxides, commonly referred to as iron sludge [6]. Oxygen has a dual impact on the corrosion process. On one hand, oxygen acts as a passivator, reducing corrosion by forming a protective film on the metal surface, oxidizing exposed areas, and creating passivating adsorption layers. On the other hand, oxygen, as an active depolarizer, can intensify corrosion by depolarizing cathodic areas [7].

With an increase in the concentration of oxygen in the solution, the corrosion rate initially increases. However, the protective effect of oxygen eventually prevails, leading to a decrease in the overall corrosion intensity. Oxygen corrosion of steel is particularly accelerated at high water flow rates, as protective films are detached from the steel surface. Therefore, it is recommended to use stable water in closed-loop and recirculating cooling and heating systems. Corrosion aggressiveness of water can be reduced through various methods, including the use of corrosion inhibitors or the prior removal of aggressive gases from water, known as water degassing [8]. These methods can be categorized chemical, biochemical, as physical, and physicochemical.

Physical methods for degassing include the thermal degassing, vacuum degassing, nitrogen purging, desorption, and membrane degassing [9–16].

Hydrazine [17] is practically capable of completely deoxygenating water, producing inert nitrogen as a byproduct.

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2$$
 (1)

This method is the most effective. However, it has the drawback of the high cost of hydrazine, which results in significant economic expenses. Therefore, this method is mainly used for the final removal of oxygen from water after physical methods.

Physical water degassing methods can be carried out in two ways. In the first case, water is brought into contact with air at near-zero partial pressure. In the second method, conditions are created to reduce the solubility of gas in water. Since the carbon dioxide pressure is close to zero, its degassing occurs during aeration [18; 19].

The deoxygenation process of water was conducted using sulfite-form anionite [20]. Desalinated water and condensate were used for research purposes. However, the more important and interesting question is the removal of oxygen from water containing hardness ions. In this case, the process will depend on the concentration of anions. Therefore, the application of redox potential of ion-exchange resin of this type can be problematic for cooling systems that use natural water without partial softening. This process was studied using AV-17-8 anionite in Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> forms when passing tap water [21].

One of the methods for deoxygenating water is the use of redoxites – modified by reducers of cationites or anionites. This method allows complete removal of oxygen ions from water without secondary contamination. The peculiarity of redoxites lies in a wide range of redox potentials due to the polymeric carrier and ionogenic groups, high redox capacity provided by a significant number of functional groups, a developed internal reaction surface for redox group fixation by a polymeric chain [22].

There is a water deoxygenation technology that is more rational from a technical and economic standpoint. It involves the use of electron-ion exchange filters, which are loaded with ionites capable of undergoing redox reactions and ion exchange reactions. Such electron-ion exchangers have gained the name "Redox filters" or "redoxites" [23; 24].

Redoxite is an organic-mineral compound made based on synthetic ion-exchange resin (e.g., cationite with metal ions of the variable valence introduced and fixed in it).

Methods for obtaining filtering loads for water deoxygenation using elements of the variable valence, abrasive materials, and during variable conditions of metal salt treatment with conversion into an insoluble state, have been described [25; 26]. This approach has led to a reduction in the solubility of iron compounds fixed on the surface and in the pores of the filtering material, preventing the leaching of iron ions from the filtering material, while simultaneously reducing the dissolved oxygen concentration in water to less than 50  $\mu$ g/dm<sup>3</sup> [27]. The initial material contains cationexchange resin in the Na<sup>+</sup> form and anionexchange resin in the Cl<sup>-</sup> form. This mixture was treated with a solution of iron sulfate (II) with sodium thiosulfate and alkali to convert the metal into an insoluble state [28].

There is also active development in the direction of deoxygenation using biologically synthesized nanoporous loads on silicates and carbon [29; 30].

In the work [31], a new technology for chemical deoxygenation of water using a monosolution of  $Na_2SO_3$  in a stoichiometric amount, at a concentration of 10-15 %, followed by filtration through a Redox catalytic filter, was proposed. The catalytic filtering material used in

this case is redoxite. Production studies have shown the effectiveness of this technology.

However, all these methods require the regeneration of spent redoxites.

This study aimed to determine the effectiveness of water deoxygenation with ironcontaining composites based on redoxites while reliably controlling the iron compound content in the deoxygenated water. The research focused on environmentally safe heating systems and steam and electricity production systems.

The research objectives included:

- evaluating the effectiveness of new ironcontaining composites in deoxygenating tap water and sodium-cationized water;

- determining the conditions for removing iron compounds from deoxygenated tap water and softened water;

- establishing the dependence of deoxygenation and iron removal efficiency on the filtration rate through the redox filter.

## Materials and methods

The study suggests using a modified load based on iron-containing composites (ironcontaining sorbent) as a reducer. This material is readily available, obtained from industrial waste, and in case of its decreased activity, the problem can be solved by replenishing with additional quantities of iron-containing sorbent.

Oxygen removal processes from water were conducted using the iron-containing sorbent (Fig.1a) and a filtering load consisting of sequential filtration through a column filled with an iron-containing composite and a column filled with cationite Ky-2-8 in the Na<sup>+</sup> form (Fig.1b) (V<sub>i</sub> = 50 cm<sup>3</sup>). The setup diagram is presented in Figure 1.

Tap water (H = 4.9 mg-eq/dm<sup>3</sup>; A = 4.9 mg-eq/dm<sup>3</sup>; [Ca<sup>2+</sup>] = 3.9 mg-eq/dm<sup>3</sup>; pH = 7.500; [Cl<sup>-</sup>] = 35.1 mg/dm<sup>3</sup>; [SO<sub>4</sub><sup>2-</sup>] = 27.5 mg/dm<sup>3</sup>) was filtered at a flow rate of 1.50–7.50 m/h. Sodium-cationized water (H = 0.0 mg-eq/dm<sup>3</sup>; A = 4.9 mg-eq/dm<sup>3</sup>; pH = 7.770) was filtered at a flow rate of 1.50–7.50 m/h.

Water samples were collected after passing through the column filled with the ironcontaining sorbent. The residual oxygen content (instrument Milwaukee MW600), iron (instrument Milwaukee MW14), and pH of the medium (instrument pH-150 Mi) were determined in the water.

Water was passed through the filtering load. Residual concentrations of oxygen, iron, pH of the medium, and residual water hardness were determined in the collected samples.



#### **Results and Discussion**

Tap water from Kyiv was passed through a column loaded with the iron-containing sorbent. The oxygen content before and after the

experiment, the total iron content, and the total water hardness were determined. The results of deoxygenating tap water with the iron-containing sorbent are shown in Figures 2 and 3:



Fig. 2. Dependency of dissolved oxygen concentration (1; 2) and iron concentration (3; 4) on the volume of tap water ([O<sub>2</sub>] = 6,10 mg/dm<sup>3</sup>; H = 4,90 mg-eq/dm<sup>3</sup>; pH = 7,71) passed through the iron-containing sorbent (1; 3) and filtration media (2; 4). Filtration rate – 1.50 m/h



Fig. 3. The dependence of pH (1; 2) and hardness (3) on the volume of passed tap water ( $[O_2] = 6.10 \text{ mg/dm}^3$ ; H = 4.90 mg-eq/dm<sup>3</sup>; pH = 7.71;) through the iron-containing sorbent (1; 3) and filtration media (2). Filtration rate – 1.50 m/h

Through contact with dissolved oxygen in water, the oxygen concentration decreases from approximately 6.10 to 0.87 mg  $O_2/dm^3$ , which is a 7.01-fold reduction. However, this method has

certain drawbacks. Water additionally becomes contaminated with iron ions, the average content of which is 0.75–0.77 mg/dm<sup>3</sup>, and the water

hardness remains at the initial level (H =  $4.9 \text{ mg-eq/dm}^3$ ).

Therefore, the water was subsequently passed through a filtering load to prevent secondary contamination with iron ions. Samples were taken in 2 dm<sup>3</sup> portions. The samples were analyzed for oxygen content, iron ions, pH of the medium, and total water hardness. The results of deoxygenation of tap water with sequential treatment using an iron-containing sorbent and cationite KY-2-8 in the Na<sup>+</sup> form are shown in Figures 2 and 3:

When using the filtering load, the concentration of dissolved oxygen decreases from 6.10 to 0.55 mg  $O_2/dm^3$ . Ion exchange on the cationite allows for the removal of a secondary contaminant - iron - from the water. In this case, the iron concentration decreases from 0.77 to 0.09 mg/dm<sup>3</sup>. This treatment allows

reducing the water hardness to zero in the initial samples. Further, as the ion-exchange capacity of the ionite is exhausted, its concentration increases to the initial values. The increase in the efficiency of oxygen removal occurs through its binding when interacting with iron (II) cations sorbed on the cationite.

When the cationite is saturated with  $Ca^{2+}$  ions, its efficiency in sorbing  $Fe^{2+}$  ions decreases. Therefore, when the ion-exchange capacity of the ionite is exhausted by calcium ions in the solution, an increase in the concentration of iron ions is observed. Additionally, to some extent, the pH of the medium decreases (Figure 3, 5), leading to a decrease in the effectiveness of binding oxygen with sorbed iron ions. After the regeneration of the cationite with a NaCl solution, its activity increases, and it effectively removes iron (Figure 2).



Fig. 4. The dependence of dissolved oxygen concentration (1; 2; 3; 4) and deoxygenation efficiency (5; 6; 7; 8) on the volume of passed Na<sup>+</sup> cation-exchanged water ([O<sub>2</sub>] = 6.10 mg/dm<sup>3</sup>; pH = 7.770) through the filtration media at different filtration rates, m/h: 1.50 (1; 5); 3.00 (2; 6); 4.50 (3; 7); 7.50 (4; 8)



Fig. 5. The dependence of iron concentration (1; 2; 3; 4) and pH (5; 6; 7; 8) on the volume of passed Na<sup>+</sup> cationexchanged water ( $[0_2] = 6.10 \text{ mg/dm}^3$ ; pH = 7.770) through the filtration media at different filtration rates, m/h: 1.50 (1; 5); 3.00 (2; 6); 4.50 (3; 7); 7.50 (4; 8)

Usually, in heating systems and when supplying water to water heaters and steam boilers, softened or desalinated water is used. Therefore, sodium-cationized water was used, involving a two-stage water treatment process: water softening on cationite KY-2-8 and deoxygenation using filtering load. Samples were taken in 1 dm<sup>3</sup> portions. The water was analyzed for oxygen content, iron, and medium reaction. The results of deoxygenation of Na<sup>+</sup> cationized water on the filtering load are shown in Figures 4 and 5. During the deoxygenation of sodiumcationized water, in which hardness ions are absent, the dissolved oxygen concentration is approximately 0.30 mg  $O_2/dm^3$ , and the residual iron concentration averages 0.05 mg/dm<sup>3</sup>. Separate removal of hardness ions and iron from ionites allows obtaining separate exhausted regeneration solutions that can be easily processed.

Since the process of deoxygenation of water occurs as a result of a chemical reaction - the oxidation of iron compounds, it was reasonable to conduct research to determine the dependence of the effectiveness of water deoxygenation on the filtration rate through the load. The filtration rate varied from 1.50 to 7.50 m/h. The filtration rate significantly affects the effectiveness of deoxygenation and the removal of the secondary contaminant - iron ions from the water. The efficiency of removing compounds depends linearly on the filtration rate. With an increase in the filtration rate by 2.0–3.0 times, the oxygen content increases from 0.30 to 0.60-0.90 mg/dm<sup>3</sup>, which is an increase of 2.0-3.0 times. With an increase in the filtration rate to 7.5 m/h, the oxygen content increases almost 5 times (from 0.30 to 1.51 mg/dm<sup>3</sup>). The same tendency is observed in the processes of iron ion removal. The iron content increases from  $0.05 \text{ mg/dm}^3$  to  $0.25 \text{ mg/dm}^3$  as the filtration rate increases from 1.50 to 7.5 m/h.

The use of an iron-containing sorbent ensures effective removal of oxygen from water. When

treating tap water with an iron-containing sorbent, a deoxygenation level of 87 % was achieved at a filtration rate of 1.50 m/h with a loading volume of 50 cm<sup>3</sup>. Of course, with such a loading volume, the contact time of water with the sorbent is very short to ensure complete oxygen binding. However, when using a filtering load, the deoxygenation level increased to 95 % with practically complete removal of iron from the water. In the case of using sodium-cationized water and two-stage filtration, the deoxygenation level reached 97 %. Clearly, by increasing the volume of loading with an iron-containing sorbent, complete deoxygenation of water can be achieved.

The fact that the effectiveness of water deoxygenation decreases with an increase in the filtration rate only confirms that at a constant rate of interaction of the iron-containing sorbent 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 loading with an iron-containing sorbent. Therefore, in further studies, the optimal ratios between the volume of loading with redoxite, filter diameter, and redoxite layer height will be determined at selected filtration rates.

The influence of the environment's pH on the process efficiency was determined. An increase in the environmental pH from 7.77 to 9.75 results in a decrease in oxygen binding efficiency. With an increase in filtration rate and environmental pH, the iron concentration in the water rises.



Fig. 6. The impact of the environmental pH and filtration rate on the iron concentration of the filtered Na<sup>+</sup> cationexchanged water through the filtration media was studied

In the figure 7 – presented typical technological scheme of using the researched method. It can also be supplemented with waste processing technologies and regeneration solutions.



Fig. 7. Technological scheme (I - water intake for preparation; II - outlet of purified water for further use; 1 - tank with water for preparation; 2 - pump; 3 - microfiltre; 4 – redox column; 5 – cationite column; 6 - tank with purified water)

## Conclusions

The efficiency of water deoxygenation using an iron-containing sorbent has been determined, which allows reducing the concentration of dissolved oxygen in water from  $6.1 \text{ mg } O_2/\text{dm}^3$  to 0.87 mg  $O_2/\text{dm}^3$ , which is 7 times lower. The drawback of this process is the secondary contamination of water with iron ions (0.77 mg/dm<sup>3</sup>).

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During the deoxygenation of water and its subsequent sodium-cationization, the dissolved oxygen content in the water decreases to  $0.57 \text{ mg } O_2/\text{dm}^3$ , and secondary contamination of water with iron ions does not occur.

The influence of filtration rate on the processes of water deoxygenation and iron ion removal has been investigated. A linear inverse relationship between the efficiency of compound removal and the filtration rate has been demonstrated.

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