1. Introduction

The problem of providing population and industry with water becomes more important with every year. Water scarcity is especially felt in regions with a significant quantity of industrial enterprises, specifically the southern and eastern areas of this country. The main measures for improving the situation imply better use of water resources, development and application of highly effective methods for water conditioning and purification.

Most of the water used in the industry is spent in the cooling systems and in the processes of energy generation. Thus, it is necessary to pay special attention to the improvement of water conditioning technologies for circular and closed water-circulating systems. The use of such systems makes it possible to reduce the volume of fresh water intake. In addition, such systems reduce anthropogenic load on the water reservoirs through the minimization of discharges.

The use of water-circulating systems in industry is limited due to high requirements to the quality of water. First of all, in terms of hardness and aggressiveness of water. The presence of ions of rigidity and dissolved gases in water causes corrosion of metal and deposition of the scale-formation products on the walls of equipment. This in turn leads to frequent replacement of elements in the system and results in a significant increase in the cost of operation and repair of equipment.

In order to prevent corrosive processes, the inhibitors of metal corrosion are applied [1]. Most often, water-circulating systems use phosphorus-containing compounds as inhibitors [2]. However, among a large list of benefits, there are a number of drawbacks when applying corrosion inhibitors, specifically: the toxicity of reagents, biological, chemical and thermal instability.

Recently, it has been increasingly popular at enterprises to employ a technique for reducing corrosion aggressiveness of water in closed water-circulating systems through preliminary deoxygenation using redoxites – ionites, modified with reducing agents. However, the effectiveness of applying a given method depends, first of all, on the shape and type of the modified ionite and composition of the starting water.

Thus, the problem of the protection of water-circulating systems from corrosion processes remains relevant. One of the far-reaching directions in the protection of closed water-circulating systems against corrosion is the preliminary deoxygenation of water with the use of redoxites.
it is required to reduce the concentration of oxygen in water, it is necessary to perform, after the deaerator, additional deoxygenation of water using one of the methods from [4].

Most often, the processes of water deoxygenation involve chemical degassing with the use of such reducing agents as hydrazine, sodium sulfite, sulfur dioxide [5]. This method makes it possible to deoxygenize water almost completely. However, treatment of water with reagents has a few disadvantages. For example, when applying sulfur dioxide, at first there forms sulphurous acid that is easily oxidized to sulfuric acid, which significantly lowers pH of the medium. Sodium sulfite during water deoxygenation turns into sodium sulfate, that is, the concentration of sulfates grows.

In the case of applying hydrazine, water deoxygenation is accompanied by the formation of nitrogen (N₂) [6]. However, this reagent also has several drawbacks, including high cost and toxicity. In addition, the result of thermal decomposition of excessive hydrazine is the formation of hydrogen and ammonia in the system. The latter accelerates corrosion of water-circulating systems.

It is also possible to apply for the deoxygenation a technique for blowing the water with such gases as nitrogen (N₂) and carbon dioxide (CO₂) using a rotor-stator reactor [7].

Membrane methods have some advantages over the chemical and physical methods for water deoxygenation. Non-porous composite PDMS membranes made of polydimethylsiloxane with silicon dioxide grids, obtained by the method of sol-gel deposition, demonstrated remarkable characteristics in the course of water deoxygenation. They have significant benefits for industrial use in the processes of water deoxygenation [8] [9].

In order to remove dissolved oxygen from water, membrane systems with vacuum degassing are also applied [9], as well as vacuum degassing utilizing an inert gas (N₂) [10]. However, the efficiency of membrane methods during water deoxygenation depends on the type of a membrane module, starting concentration of oxygen in water, water flow rate [8–10], concentration of nitrogen in the flows of inert gas and nitrogen [10], and the vacuum level [8].

An alternative technique for water deoxygenation is the process of bioactive deoxygenation based on yeast. Research results confirm the feasibility of a given method to treat ballast waters of marine vessels even at a temperature below 2 °C without any risk of increasing water toxicity. However, water treatment time when using this method is long enough [11].

In the energy sector, as well as in the industrial water-circulating systems, the most promising method to remove aggressive gases from water is the technique that employs redoxites. When the redox filters are applied, water deoxygenation proceeds effectively, bringing down economic cost of the process, as well as ensuring high quality of water.

Redoxites are obtained based on the ion-exchange resins by treating them with polyvalent metals. The authors of [12] established a dependence of water deoxygenation efficiency on the type of cationite and the technique of its modification.

Given their combination of redox and ion-exchange properties, the electro ion exchangers are used as the redox sorbents of oxygen in water conditioning processes [13].

The deoxygenation of solutions is typically performed applying redox sorbents based on copper. In paper [14], authors examined the kinetics of oxygen removal on a grain copper-containing electro ion exchanger, which is composed of an ion exchange resin and nano-dispersed copper, spatially distributed in the ionite. A mathematical notation was subsequently given for the macro kinetics and dynamics of the oxygen redox-sorption by nano-composites based on the ionite and nano-dispersed metals [15].

Authors of [16], based on the fibrous ionites, synthesized palladium-containing catalysts for the processes of water deoxygenation. Results of this study prove that the nature and physical-chemical properties of the carrier affect the reduction of the active component.

In the case when water contains ions of hardness, it is more expedient to use redoxites based on anionites in the sulfite form [17]. Since the process in this case depends on the anions only, the stage of preliminary softening of water is not required.

However, water deoxygenation on the anionite depends on the desorption of a reducing agent in the presence of competing anions [18]. It was shown that the anionite AV-17-8, modified with sulfites, is expedient to apply for the deoxygenation of waters that contain anions in the amount not exceeding 6 mg-equiv./dm³.

The prospect of using redoxites in the processes of water deoxygenation is determined, first of all, by the possibility of anion modification, as well as the reducing capacity, reliability, and operation time.

3. The aim and objectives of the study

The aim of present study is to determine conditions for improving the sorption capacity of anionites for sulfite- and bisulfite-anions in order to enhance the efficiency of using ionites in the processes of water deoxygenation.

To accomplish the set aim, the following tasks have been solved:

- to identify conditions for the above-the-equivalent sorption of sulfite-anions on the high-base anionites in the salt and basic forms;
- to establish a dependence of capacity of the weakly-acidic anionites in the salt and basic forms on the concentration of solutions of sulfite and sodium bisulfite;
- to estimate the effect of the anions dissolved in water on the resource in using anionites modified with sulfites.

4. Materials and methods for studying the processes of water deoxygenation

In order to obtain the reagents, we used in the present study the low-base anionites Dowex Marathon WBA, AMBERLITE IRA 96, and the high-base anionite AB-17-8.

In the course of present research, we used solutions of sulfite, sodium bisulfite in concentrations ranging from 1 to 11 %, chloride- and sulfate-containing solutions with concentrations ranging from 30 to 110 mg/dm³. The study was carried out under normal temperature conditions.

The processes of sulfite sorption on the anionites were investigated using the following procedure. We passed through the anionites AB-17-8, Dowex Marathon, AMBERLITE IRA96 in the Cl⁻, OH⁻, SO₃⁻ form, of volume 20 cm³ or 50 cm³, placed in the column with a diameter of 19–30 mm, 250–650 cm³ of solutions Na₂SO₃, with a concentration of 1 %, 3 %, 5 %, 6 %, 8 %, 10 %, 11 %, or NaHSO₃, with a concentration of 1 %, 3 %, 5 %, 6 %, 8 %, 10 %. Filtration rate was 8–10 cm³/min. By taking the samples of filtrate with
a volume of 50 cm³, we determined the residual content of sulfite-anions.

Total exchange dynamic capacity was determined from formula (mg-equiv./dm³)

\[
TEDC = \frac{(C_i - C_m)}{V} V',
\]

(1)

where \(C_i\) is the starting concentration of ions in the solution, g-equiv./dm³; \(C_m\) is the concentration of ions in the \(i\)-th sample after sorption, g-equiv./dm³; \(V\) is the sample volume, dm³; \(V'\) is the volume of ionite, dm³.

The processes of sulfate desorption on resin beads were studied in line with the following procedure. We passed the anionites AB-17-8 and Dowex Marathon in the SO₃⁻ form, a volume of 20 cm³, placed in the column with a diameter of 19–30 mm, 2,000 cm³ of solutions NaCl, with concentrations ranging from 41 mg/dm³ to 110 mg/dm³, or Na₂SO₄, with concentrations ranging from 31 mg/dm³ to 70 mg/dm³. Filtration rate was 8–10 cm³/min. By taking the sample of filtrate with a volume of 200 cm³, we determined the content of chlorides or sulphates and the content of sulfate-anions.

5. Results of research into obtaining redoxites by the modification of anionites

The modification of anionites was performed by converting the latter into sulfite form from the chloride, sulfate, and basic forms. The processes of modification of the high-base anionite in the chloride form are characterized by the data shown in Fig. 1.

![Fig. 1. Dependence of concentration of sulfite-anions in the solutions of sodium sulfate, at concentrations, %; 3 (4), 6 (3), 8 (2), 10 (1), on the volume passed through the anionite AB-17-8 (V=50 cm³) (EDC, mg-equiv./dm³; 2,416 (1), 1,550 (2), 1,884 (3), 930 (4))](image)

It is known that during water deoxygenation sulfite-anions sorbed on the anionite are oxidized to sulfate anions. Therefore, in order to further use the anionite during regeneration, there arises a problem of converting it from the sulfate to the sulfite form. The effectiveness of this process can be estimated by the results shown in Fig. 2.

The above-equivalent sorption of sulfite-anions in this case is predetermined by the high concentration of sulfites in the modified solution. In this case, the sorption of ions in the form \(\text{SO}_3\text{Na}\) is possible, which ensures the sorption that is two times higher compared with ions of \(\text{SO}_4\text{Na}\).

Next, given the simplicity of converting the low-base anionites into basic form, we employed such low-base anionites in the research as: Dowex Marathon WBA and AMBERLITE IRA 96. The anionites were used in the chloride and basic form.

The curves of sulfite sorption on the anionite Dowex Marathon WBA are shown in Fig. 3.

![Fig. 2. Dependence of concentration of sulfite-anions in the solution of sodium sulfate with a concentration of 10 % while filtering it through the anionite AB-17-8 (V=20 cm³) in the salt (SO₃⁻) form (EDC=4,238 mg-equiv./dm³)](image)

![Fig. 3. Dependence of the concentration of sulfites (1–4) on the volume of solutions of sodium sulfate passed through the anionite Dowex Marathon WBA in the Cl-form (V=20 cm³) with concentration, %: 3 (4), 6 (3), 8 (2), 10 (1) (EDC, mg-equiv./dm³; 1,545 (1), 1,890 (2), 1,225 (3), 1,025 (4))](image)

We used the following starting concentrations of sodium sulfate solutions: 10 %, 8 %, 6 %, and 3 %. EDC was, respectively, 1,545 mg-equiv./dm³, 1,890 mg-equiv./dm³, 1,225 mg-equiv./dm³, and 1,025 mg-equiv./dm³.

Sorption capacity of the anionite AMBERLITE IRA 96 in the Cl-form can be estimated by the results shown in Fig. 4, 5. Sorption of sulfite-anions on the anionite AMBERLITE IRA 96 in the Cl-form was performed from the NaSO₄ solutions with a concentration of 10 %, 8 %, 6 %, and 3 %. EDC of the anionite AMBERLITE IRA 96 is close to EDC of Dowex Marathon and is, respectively, 1,640 mg-equiv./dm³, 1,700 mg-equiv./dm³, 1,460 mg-equiv./dm³ and 780 mg-equiv./dm³, depending on the concentration of solution of Na₂SO₄.

![Fig. 4. Dependence of the concentration of sulfites (1–4) on the volume of sodium sulfate passed through the anionite AMBERLITE IRA 96 in the Cl-form (V=20 cm³) with concentration, %: 3 (4), 6 (3), 8 (2), 10 (1) (EDC, mg-equiv./dm³; 1,640 (1), 1,690 (2), 1,460 (3), 780 (4))](image)

In addition, we conducted research on the anionite AMBERLITE IRA 96 in the OH-form during sorption from the solutions of NaHSO₃ (Fig. 5) with starting concentrations: 10 %, 8 %, 6 %, and 3 %. In this case, EDC was, respectively, 4,790 mg-equiv./dm³, 4,340 mg-equiv./dm³, 4,240 mg-equiv./dm³, 3,660 mg-equiv./dm³ for the anionite volume of 20 cm³.
Dowex Marathon WBA in the sulfite form (Fig. 7, 8).

Sulphates, or are not washed out at all.

are immediately oxidized by the oxygen, present in water, to

that sulfites are either washed out in a meager quantity and

selected samples (Fig. 6). This can be explained by the fact

concentration of 1 % and 5 %. Sulfite desorption did not take

in the amine form with solutions of sodium bisulfite with a

We obtained ionite in the sulfite form when treating anionite

investigated the processes of desorption of sulfite-anions

water at which sulfites are washed out of the anionite, we

Fig. 7. Change in the concentration of chloride-anions

(1–4) with the passed volume of NaCl solution with concentration,

mg/dm³: 52.5 (1); 102.8 (2); 41.1 (3); 95.7 (4),

through the anionite Dowex Marathon WBA (V=20 cm³),

with capacity for sulfites, mg-equiv./dm³:

5,070 (1), 4,380 (2), 3,428 (3), 3,393 (4)

In the study of processes of desorption of sulfite-anions,

used sodium chloride solutions with a concentration of

41.1–102.8 mg/dm³. At the initial stage, there is a slight sorption of chlorides at their starting concentrations 95.7

and 102.8 mg/dm³, which leads to the washing out of sulfi-

e-anions from the anionite.

Sulfate sorption on a given anionite in the sulfite form

can be estimated in Fig. 8. Despite the fact that the sulfites

were almost not washed out from the ionite, a partial sorp-
tion of sulfates did occur.

In this case, as was the case for chlorides, there are no

sulfites in solutions. At least the method of iodometry failed

to identify them.

We also investigated the processes of sorption of sulfates

and chlorides on the low-base anionite in the sulfite form at

exchange capacity for sulfites 330–550 mg-equiv./dm³ (Fig. 9).

Fig. 9 shows that at the beginning of the process there

occurred a partial sorption of chlorides and sulfates. In this

case, desorption of sulfites was not observed. Thus, the sorp-
tion of sulfites and chlorides can be explained by the filling

of the vacant capacity of the anionite.

6. Discussion of results on the sorption and desorption

of sulfites on redoxites

The redoxites obtained through the modification of anionites

using sulfites possess high reducing capability and do not lead

to secondary contamination of water with desorbed substances.
Redoxite in the sulfite form is easily obtained when treating the high-base anionite AB-17-8 in various forms with solutions of sodium sulfite (Fig. 1). Thus, EDC reaches 1,500–2,400 mg-equiv./dm³ for the case of using 6–10% solutions of sodium sulfite.

The low-base anionites Dowex Marathon WBA and AMBERLITE IRA 96 in the Cl⁻-form are characterized by a low capacity for sulfite-anions compared with AB-17-8. For the solutions of sodium sulfite with starting concentrations in the range of 3–10%, EDC of Dowex Marathon WBA is 1,025–1,890 mg-equiv./dm³, and for AMBERLITE IRA 96 ~ 780–1,700 mg-equiv./dm³ for the ionite volume of 20 cm³.

Low capacity of a given redoxite can be explained by the low volume of ionite, short time of contact with water, as the capacity greatly depends on the kinetic factors. Fig. 3 also shows that the capacity of ionite depends on the concentration factor.

Capacity of the ionite AMBERLITE IRA 96 when using NaHSO₃ is much larger compared with Na₂SO₃.

This is confirmed by the capacity of ionite relative to these solutions and is explained by the following:

\[ 2\text{An}^+\text{Cl}^- + \text{Na}_2\text{SO}_3 \leftrightarrow \{\text{An}^-\} \cdot \text{SO}_4^{2-} + 2\text{NaCl} \]  

(1)

\[ \text{An}^-\text{OH}^- + \text{NaHSO}_3 \rightarrow \text{An}'\text{NaSO}_4^+ + \text{H}_2\text{O}. \]  

(2)

When using anionite in the salt form (reaction 1), during sorption of sulfites at high concentrations of sulfite-anions, chloride-anions enter the solution, which causes acceleration of the reverse reaction. In addition, the above-equivalent sorption is insignificant. In the interaction between anionite in the amine form and sodium bisulfite solutions the process proceeds with the formation of water as a byproduct of the reaction with the sorption of two equivalents of sulfite per one equivalent of the anionite capacity. In this case, An'NaSO₄⁺ is formed (reaction 2). This is exactly the main reason for the high capacity of anionite for sulfite-anions.

In thermal engineering, circulating heating systems often use water obtained through the Na⁺-cationation. Natural waters typically have low concentration of chlorides and sulphates. However, when using mineralized water, the concentration of these anions can be significant. Under these conditions, there may occur a partial desorption of sulfites from the modified anionite, which would lead to a decrease in the resource of its application at water deoxygenation.

Fig. 6 (curves 1–4) shows there is a certain decrease in the content of chloride- and sulfate-anions. The main reason for this is the removal of these anions from water through sorption. The sorption, however, could occur not due to the desorption of sulfites but rather at the expense of filling the vacant exchange capacity of anionite, which was not used at its conversion to the SO₄²⁻ form. That is why, when removing sulfates and chlorides from water, there obviously occurs the desorption of hydroxide anions.

When using the low-base anionite Dowex Marathon WBA, the washout of sulfite-anions is noticeable only at the concentration of chlorides of 102.8 mg/dm³, which is predetermined by the above-equivalent capacity of anionite for sulfites (≈4,380 mg-equiv./dm³).

When treating redoxite in the sulfite form with sodium sulfate solutions (Fig. 8, curves 1, 2), the capacity of anionite for sulfites was quite high. However, during experiments we observed sulfate sorption without substantial desorption of sulfites. In this case it could be possible that there occurred the formation of complex anions of the type \([\text{SO}_4^{2-}\text{Na}_2\text{SO}_4\text{Na}^-]\). It is not possible to explain the sorption of sulfates in solutions though the oxidation of sulfites, because sulfates would have formed at the oxidation of sulfites with the concentration of the former remaining constant.

In general, based on the results obtained, we can argue that anionites in the sulfite form, especially at the above-equivalent sorption of the latter, are quite sensitive to the presence in water of other anions – chlorides and sulphates. Therefore, the modified anionites are better to use for the treatment of desalinated water.

6. Conclusions

1. It is shown that the sorption of sulfite-anions on the high-base anionites in the salt form depends on the concentration of sodium sulfite solution. The capacity of ionite for sulfite-anions increases to 4,200 mg-equiv./dm³ with an increase in the concentration of sodium sulfite to 10% regardless of the salt form of anionite – chloride or sulfated.

2. It was established that during treatment, under dynamic conditions, of weakly-acidic anionites in the salt form and the basic form with solutions of sodium bisulfite and sulfite, the capacity for sulfites increases with the increase in the concentration of solutions. As a result of the above-equivalent sorption, the capacity for anionite in some cases reaches 5,000 mg-equiv./dm³.

3. We determined the effect of anions, dissolved in water, which is deoxygenated, on anionites in the sulfite form. It is shown that sulfates and chlorides are to some extent removed from water with a partial, sometimes insignificant, desorption of sulfite-anions. Therefore, in order to enhance resource of the obtained redoxites, modified with sulfites, it is expedient to use desalinated water or water with a low content of chlorides and sulphates.

References


