

## Development of New Water Deoxidization Systems for Heat and Power Plants

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### ABSTRACT

The analysis of water conditioning methods for closed water supply systems was carried out in the work. The expediency of using redoxites based on ion exchange materials to combat the corrosion processes in water recirculation systems by preliminary deoxidation of water was shown. Modified KU-2–8, Dowex Mac-3, AB-17–8, Dowex Marathon WBA, AMBERLITE IRA 96 ion exchange resins were used as deoxidizing materials.

**Keywords:** redoxite, ion exchange resin modification, deoxidation, ion exchange resin.

### INTRODUCTION

The problem of providing the population and industry with water is exacerbated every year around the world. The regions with a significant number of industrial enterprises are particularly acutely deficient. The main measures to improve the situation are better use of water resources, creation and application of highly efficient methods of air conditioning and water treatment. Most of the water in industry is used in the cooling and energy systems. Therefore, special attention should be paid to the improvement of water conditioning technologies for reversible and closed water circulation systems. Using the above-mentioned systems, the fresh water intake can be reduced. In addition, such systems reduce the anthropogenic load on water bodies by minimizing discharges.

Restrictions on the use of water circulation systems in industry are due to high water quality requirements. First of all, these concern the hardness and aggressiveness of water. The presence of salts in the water causes corrosion of metals and deposition of scale products on the walls of the

equipment. This, in turn, leads to frequent replacement of system elements, and, as a result, significantly increases the cost of operation and repair of equipment. Metal corrosion inhibitors are used to prevent the corrosion processes [Cervova et al., 2014, Nosachova et al. 2020]. The phosphorus-containing compounds are most often used as inhibitors in water circulation systems [Chichenin et al., 2015]. However, among the large list of advantages, there are a number of disadvantages in the case of corrosion inhibitors, namely: toxicity of reagents, as well as biological, chemical and thermal instability [Nosachova et al., 2020].

Recently, the method of reducing the corrosive aggressiveness of water for closed water circulation systems by pre-deoxidation with the use of redoxites, i.e. ion exchangers modified with reducing agents – has become increasingly popular at enterprises. Especially important is the deoxidation of energy water used to produce steam and water supplied to the heating network. The effectiveness of this method depends primarily on the shape and type of modified redoxite and the composition of the source water.

Today, there are various methods of water treatment stabilization on an industrial scale. According to the method of execution, these methods can be divided into: electrochemical, sorption, reagent, physical and ion exchange. All of them are used in the preparation of water for a particular process in order to remove interfering substances. The most important fact of iron corrosion in water is dissolved oxygen. In addition, in the return pipelines of the condensate of heating systems, free carbon dioxide also affects the corrosion of metals. The degree of free oxygen removal, to prevent serious corrosion, depends on the side temperature and, to a lesser extent, on the amount of water that passes through the system.

In cold water supply systems, it is desirable that the oxygen content does not exceed  $0.2 \text{ mg} \cdot \text{dm}^{-3}$ . If it is necessary to achieve a lower content, which is not possible with one-stage deaeration, an additional chemical treatment of the water coming from the deaerator is applied [Medvediev et al.]. Chemical degassing involves the introduction of substances into the water that bind dissolved oxygen. This may be sulfur dioxide, sodium sulfide or hydrazine [Zhao et al., 2017]. When using sodium sulfite, the sulfide is oxidized to sulfate by dissolved oxygen. When using pure gas, pure acid is formed, which is oxidized to sulfuric acid by the oxygen dissolved in water.

Hydrazine allows deoxidizing the water almost completely. At the same time, oxygen binds to the release of inert nitrogen  $\text{N}_2$  [Ting et al., 2015]. The disadvantage of using hydrazine is, firstly, the high cost of the reagent, and, secondly, the high toxicity. In addition, when hydrazine is introduced into the feed water, it interacts with metal oxides, which are inevitably present in the steam-water tract with the formation of by-products. Ammonia ( $\text{NH}_3$ ) and hydrogen ( $\text{H}_2$ ) are formed in the heat carrier during the thermal decomposition of excess hydrazine hydrate. The increased content of ammonia (more than  $1000 \text{ } \mu\text{g} \cdot \text{dm}^{-3}$ ) in the condensate significantly activates the corrosion destruction of equipment, especially in the presence of oxygen. Therefore, hydrazine is used mainly for the final removal of oxygen from water.

One of the promising directions of the stabilization treatment of water for use in industry and energy, as well as for the extraction of corrosive gases dissolved in water, is the use of water. The use of redoxites will make it possible to carry out the deoxidation process more efficiently, as well

as reduce the economic costs of operating the pre-treatment equipment by replacing the existing one, including the deaerators of the thermal and vacuum conditions.

There are known methods of obtaining redoxites on the basis of ion-exchange materials with the application of metals with variable valence to their surface. In the works [Martić et al., 2015; Lafontaine et al., 2014; Tamazashvili et al., 2011; Kipriyanova et al., 2010; Polyanskiy et al., 2012] shows the prospects of their use as a load for the extraction of dissolved oxygen and other oxidants. When using ion exchangers for deoxidation, it is possible to successfully solve other problems, for example, to carry out the most various redox reactions for the treatment, purification and removal of chemical substances. The expediency of their application for the synthesis of inorganic and organic compounds in electro- and analytical chemistry is shown.

In the works [Polyanskiy et al., 2014; Egizarov et al., 2013; Tamazashvili et al., 2015;] a new approach of sulfite water treatment for oxygen extraction was considered. The authors proposed to replace soluble reagents with a solid water-insoluble sorbent modified with sodium sulfite. The use of this sorbent is promising for the removal of oxygen from water containing hardness ions. In this case, the process will first of all depend on the anions. Therefore, the use of redox potential of ion-exchange resin of this type can be promising for the cooling systems where natural water is used without partial softening. This process was investigated by the authors [Homelia et al., 2012] using the AB-17-8 anion exchange resin in  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  forms when passing water. In the process, sulfites, sulfates, chlorides, carbonates, hydrocarbons, and oxygen were controlled.

The aim of the research was to study the methods of water stabilization using redoxites based on ion exchange materials, which are used to reduce the corrosion aggressiveness of water. Their application will allow carrying out the process of water deoxidation more efficiently, as well as reducing the economic costs for the operation of water treatment equipment.

## MATERIAL AND METHODS

Modified ion exchangers were obtained by treating them with modifying reagents in a given sequence. The optimal modification conditions

were selected. Salts containing a chemical element of variable valence were used as modifiers, namely: iron (II) sulfate, sulfite, bisulfite and sodium metabisulfite.

Deposition of iron ions was performed on weakly acid Dowex MAC-3 cation exchange resin. The cation exchange resin was treated with a solution of ferrous sulfate (II) in concentrations from 1% to 10%. The flow rate of the solution was 0.12–0.18 m/h, and the volume of the resin was 20 cm<sup>3</sup>. 100 cm<sup>3</sup> of filtrate samples were taken to determine the residual iron (II) content. In order to prevent leaching of iron ions from the resin, it was treated with a solution of alkali for hydrolysis with the formation of hydroxide (Fe(OH)<sub>2</sub>).

Deposition of sulfite ions was performed on strongly-basic AB-17–8 anion exchange resin, as well as weakly-basic Dowex Marathon WBA and AMBERLITE IRA 96 anion exchange resins. Then, solutions of sulfite, bisulfite and sodium metabisulfite in concentrations from 1% to 10% were passed. The transmission rate was 0.12–0.18 m / h, and the volume of the resin was from 20 cm<sup>3</sup> to 50 cm<sup>3</sup>. Afterwards, 100 cm<sup>3</sup> of filtrate samples were taken to determine the residual sulfite content.

The full dynamic exchange capacity was calculated by the formula:

$$\text{FEDC} = \frac{\sum(C_{\text{init}} - C_i) \cdot V_s}{V_i} \quad (1)$$

where:  $C_{\text{init}}$  – initial concentration of ions in solution, mg-eq/dm<sup>3</sup>;

$C_i$  – the concentration of ions in the  $i$ -th sample after sorption, mg-eq/dm<sup>3</sup>;

$V_s$  – sample volume, dm<sup>3</sup>;

$V_i$  – volume of ion exchange material, dm<sup>3</sup>.

Deoxidation of waters of different composition was performed by filtering them through redoxite ( $V_i = 20 \text{ cm}^3$  or  $50 \text{ cm}^3$ ), placed in a column with a diameter of 19–30 mm. The filtration rate ranged from 2.12 to 10.6 m/h.

The treated water was passed through a Winkler flask, analyzing the oxygen content of each cubic meter of water passed. In addition, the reaction medium, and the content of iron or sulfite ions in the filtrate were periodically determined.

The regenerative capacity for oxygen was calculated by the formula:

$$\text{EC}_{\text{O}_2} = \frac{\sum(C_{\text{initO}_2} - C_{i\text{O}_2}) \cdot V_s}{V_i} \quad (2)$$

where:  $C_{\text{initO}_2}$  – initial oxygen concentration in water, mg-eq/dm<sup>3</sup>;

$C_{i\text{O}_2}$  – oxygen concentration in the  $i$ -th sample, mg-eq/dm<sup>3</sup>;

$V_s$  – sample volume, dm<sup>3</sup>;

$V_i$  – volume of ion exchange material, dm<sup>3</sup>.

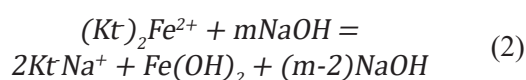
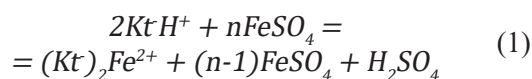
Determination of sulfites was performed by oxidizing them to sulfates with a titrating solution of iodine. The concentration of sulfate ions was determined photocolometrically with a precipitating mixture based on glycerol. The concentration of iron ions was determined photocolometrically with sulfosalicylic acid. The concentration of dissolved oxygen in water was determined by using the Winkler method [Lurie, 1986.].

## RESULTS AND DISCUSSION

### Study of the effectiveness of redoxites obtained by modification of cations with iron compounds

Redoxite modified with iron compounds is quite common in utilities during water deoxidation for heating systems. First of all, this is due to the relatively low cost of redoxite, which is used to obtain common and cheap cations and available reagent – ferrous sulfate (II), which is formed in large quantities as waste in the digestion of metal products. In this case, to prevent leaching of iron ions from the resin in the presence of hardness ions in the water, the resin is treated with a solution of alkali for hydrolysis to form a hydroxide (Fe(OH)<sub>2</sub>).

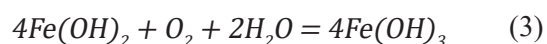
Thus, the process of obtaining redoxite is realized in two stages (reactions 1, 2):



The disadvantage of this process is the formation by reaction (1) of waste regeneration solution

containing an excess of ferrous sulfate (II) and sulfuric acid, and by reaction (2) – a solution containing an excess of alkali. Their disposal is a significant problem. This problem occurs every time after the regeneration of cation exchange resin, when after the oxidation of iron (II) hydroxide, the capacity of redoxite for oxygen is depleted.

It should be noted that iron (II) hydroxide, which is formed during hydrolysis (reaction 2), remains in the pores of the resin due to its low solubility in water. When redoxite is used, it is oxidized to iron hydroxide (reaction 3), which is also insoluble in water.

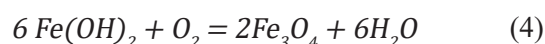


On the one hand, the use of iron (II) hydroxide as a reducing agent has a number of advantages. Its duration depends only on the concentration of oxygen in water and water consumption; it does not depend on the concentration of cations or anions in water. When the ion exchanger is used in the  $\text{Fe}^{2+}$  form, iron ions are used to bind oxygen and are also leached from the ion exchanger in the presence of hardness ions in the water, which displace the iron ions from the cation exchange resin. When using anion exchange resins in sulfite form, a significant part of the reducing agent (sulfite) is lost due to desorption from the ion exchanger in the presence of anion exchange resins in water – chlorides, sulfates, nitrates, etc.

On the other hand, iron (III) hydroxide, which is formed in the pores of ion exchanger after the

oxidation of  $\text{Fe}(\text{OH})_2$ , clogs the pores of cation exchange resin, which impairs the diffusion of ions during redox regeneration and diffusion of oxygen molecules during water deoxidation. Hence, after 6–8 filter cycles the regeneration of redoxites is inefficient. Replacement of the filter load, utilization of spent cation exchange resin significantly increases the cost of operation of redox filters of this type.

Despite the significant capacity of cations in iron ions (Table 1) [Overchenko, 2017], the reducing capacity (RC) of modified cations in both  $\text{Fe}^{2+}$ -form and ion exchangers modified with  $\text{Fe}(\text{OH})_2$  is small. This is due not only to the leaching of iron ions from the cation exchange resin by ion exchange (Fig. 2), but also to a change in the mechanism of oxygen binding by iron ions at elevated pH values (Fig. 1, Table 2). This is because at pH 8.5–9.6 during the oxidation of  $\text{Fe}(\text{OH})_2$  there is no formation of iron hydroxide (III), and magnetite (4):

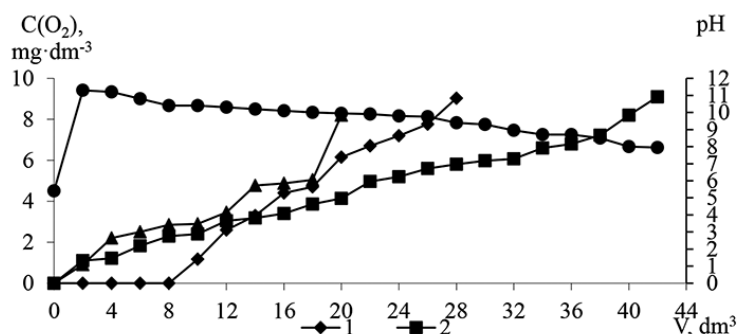


In this case, the oxidation of 1 mg-eq of oxygen consumes 3 mg-eq of iron (II), while the formation of iron hydroxide (III) requires only 2 mg-eq of iron.

In general, based on the analysis of the characteristics of redoxites obtained on the basis of cation exchange resins modified with iron compounds, it can be said that these materials should be used for deaeration of relatively small volumes

**Table 1.** Dependence of the cation exchange resins capacity on  $\text{Fe}^{2+}$  ions on their shape and composition of the solution

Ionite	Form of cation exchange resin	The composition of the solution		EC, mg-eq·dm <sup>-3</sup>
		$\text{Fe}^{2+}$ , mg-eq·dm <sup>-3</sup>	$\text{H}_2\text{SO}_4$ , mg-eq·dm <sup>-3</sup>	
Cation exchange resin KY-2-8	H <sup>+</sup>	719.42	–	2460
	H <sup>+</sup>	1079.14	–	2840
	Na <sup>+</sup>	719.42	–	1660
Cation exchange resin KY-2-8	Na <sup>+</sup>	719.42	5.0	2930
	Na <sup>+</sup>	719.42	10.0	3287
	Na <sup>+</sup>	719.42	15.0	3510
	Na <sup>+</sup>	719.42	20.0	3420
Cation exchange resin Dowex MAC-3	Na <sup>+</sup>	125.00	–	3420
	Na <sup>+</sup>	136.00	–	4560
	Na <sup>+</sup>	719.42	–	4000
Amberlit 252H	H <sup>+</sup>	719.42	–	2340
	Na <sup>+</sup>	719.42	–	2179
Purolit C150	H <sup>+</sup>	719.42	–	1540
	Na <sup>+</sup>	719.42	–	1440



**Figure 1.** Dependence of oxygen concentration (1; 2; 3) and pH of the medium (4) in tap (1), distilled (2; 4) and softened (3) water on the volume passed through the Dowex MAC-3 cation exchange resin in Fe<sup>2+</sup>- (1) and Na<sup>+</sup>-form ( $V_i=20 \text{ sm}^{-3}$ ), modified Fe(OH)<sub>2</sub> (2; 3; 4) ( $RC_1=1250 \text{ mg-eq}\cdot\text{dm}^{-3}$ ;  $RC_2=1587 \text{ mg-eq}\cdot\text{dm}^{-3}$ ;  $RC_3=951 \text{ mg-eq}\cdot\text{dm}^{-3}$ )

**Table 2.** The dependence of the renewable capacity of redoxites based on KU-2–8 on the form of the resin and its capacity for Fe<sup>2+</sup> ions in the treatment of tap water (I) and Na-cationized water (II)

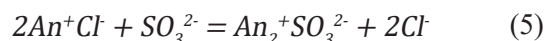
EC/RC, mg-eq·dm <sup>-3</sup>			
Fe <sup>2+</sup> -form		Na <sup>+</sup> -form, modified Fe(OH) <sub>2</sub>	
I	II	I	II
2700/1082	2850/1152	2870/1352	2900/1205

of water at high concentrations of oxygen. In other circumstances, the cost of regeneration and replacement of the filter load will be so significant that the application of the process will be unprofitable.

### Deoxidation of water on anion exchangers in sulfite form

It is known that sodium sulfite is often used for deoxidation of water by using the reagent method. The advantages of this reducing agent are its availability, low price and low toxicity. More precisely, this reagent is non-toxic, in contrast to

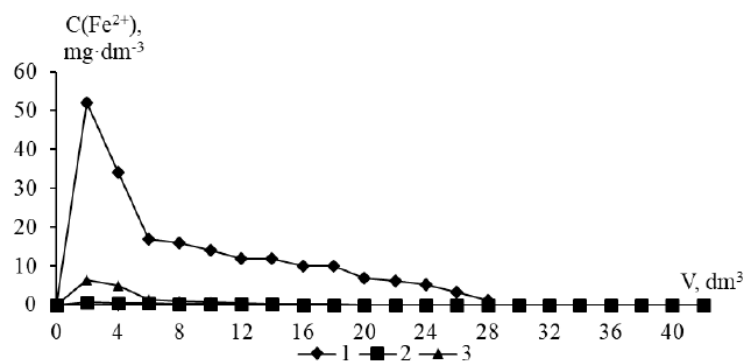
highly toxic hydrazine. The disadvantage is that sulfates are formed when oxygen binds. Sodium sulfate remains in water after the application of sodium sulfite, which is unacceptable for energy water. This disadvantage is easily avoided when using anion exchangers in sulfite form. First of all, anion exchange resins (especially highly basic ones) easily turn into a sulfite form (5):



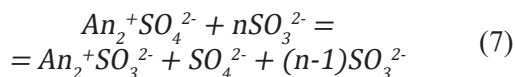
When oxygen binds, sulfite anions are converted to sulfate anions, which have a high selectivity for sorption on anion exchangers. Therefore, no ions are released into the water when dissolved oxygen binds (6).



In addition, when regenerating anion exchangers in sulfate form, they easily turn into sulfite form (7).



**Figure 2.** Initial curves of iron desorption from Dowex MAC-3 cation exchange resin in Fe<sup>2+</sup> – (1) and Na<sup>+</sup>-form ( $V_i = 20 \text{ sm}^{-3}$ ), modified with Fe(OH)<sub>2</sub> (2; 3), by passing tap (1), distilled (2) and softened (3) water

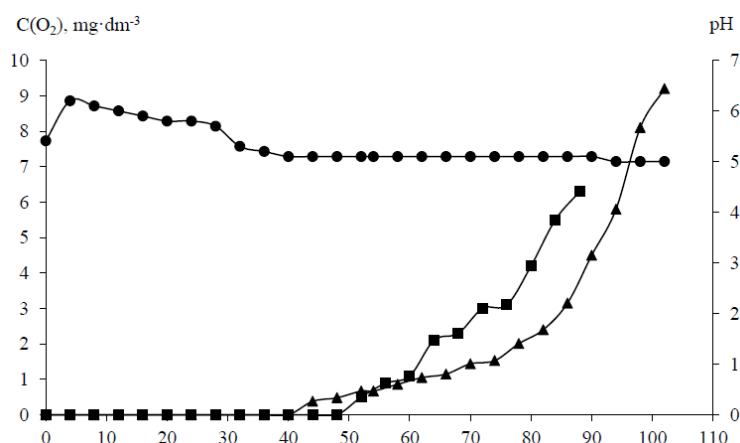
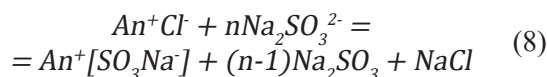


Since sulfites in solutions are easily converted into sulfates, it is easy to dispose of spent regeneration solutions. Already during storage with open air access, sodium sulfite turns into sodium sulfate. When it evaporates and dries, it is possible to obtain a product – sodium sulfate.

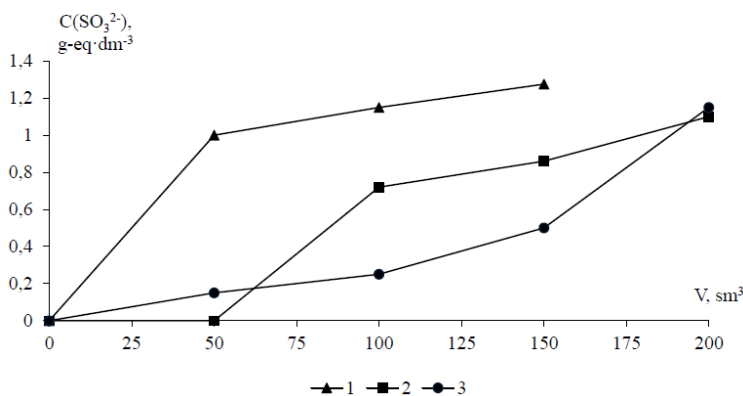
When using the AB-17–8 anion exchange resin in relatively small volumes [Overchenko, 2017], high results were obtained in the deoxidation of water (Fig. 3). The reducing capacity of redoxite reached 2129–2266 mg-eq · dm<sup>-3</sup>, which is close to the exchange dynamic capacity of the anion exchange resin for sulfite anions (Fig. 4). This indicates that the sulfite anions on the anion exchange resin react fairly quickly with the

oxygen present in the water. This allows the use of redox filters at sufficiently high filtration rates – 6–15 m/h.

It is known that anion exchangers are characterized by a relatively low capacity of anions. For AB-17–8, the capacity usually does not exceed 1800 mg-eq · dm<sup>-3</sup>. In the case of sorption of sulfite anions, the capacity of the anion exchange resin by SO<sub>3</sub><sup>2-</sup> anions reached 2129–2266 mg-eq · dm<sup>-3</sup>. This can be explained only by the equivalent sorption, given the high concentration of sodium sulfite solution used in the conversion of the anion exchange resin into SO<sub>3</sub><sup>2-</sup> form. Its concentration reached 10% or 100 g/dm<sup>3</sup>. In this case, the exchange was partly by reaction (5) and largely by reaction (8).



**Figure 3.** Dependence of oxygen concentration (1; 2) and pH (3) on the volume passed through the AB-17–8 anion exchange resin ( $V_i=50 \text{ sm}^3$ ) in  $SO_3^{2-}$ -form of distilled (1; 3) and tap (2) water ( $RC_1=2265,5 \text{ mg-eq} \cdot \text{dm}^{-3}$ ;  $RC_2=2128,7 \text{ mg-eq} \cdot \text{dm}^{-3}$ )



**Figure 4.** Initial curves of sulfite anion sorption on Dowex Marathon WBA anion exchange resin ( $V_i = 20 \text{ sm}^3$ ) in Cl<sup>-</sup>-form (1), AB-17–8 ( $V_i = 50 \text{ sm}^3$ ) in Cl<sup>-</sup>-form (2) and OH<sup>-</sup>-form (3) with 10% Na<sub>2</sub>SO<sub>3</sub> solution (1; 2) and NaHSO<sub>3</sub> solution (3) concentration 1,2 g-eq · dm<sup>-3</sup> ( $FEDC_1=1187,5 \text{ mg-eq} \cdot \text{dm}^{-3}$ ;  $FEDC_2=2360 \text{ mg-eq} \cdot \text{dm}^{-3}$ ;  $FEDC_3=2450 \text{ mg-eq} \cdot \text{dm}^{-3}$ )

Given that anion exchangers in different forms can sorb sulfite anions in different ways, as well as the fact that solutions of sulfite, bisulfite and sodium metabisulfite can be used, which also affects the processes of ion exchange, a study was conducted to study the sorption of sulfite anions.

### Study of the dependence of the capacity of anion exchange resins on sulfite anions on the conditions of their sorption

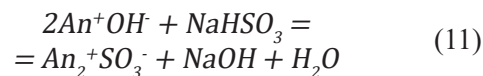
High- and low-basic anion exchangers, solutions of sulfite, bisulfite and sodium metabisulfite in various concentrations were used in the study of the sulfite sorption processes on anion exchangers. Anion exchangers were used in chloride, sulfate and basic forms. The chloride form of anion exchangers was used because, as a rule, all anion exchangers are made in chloride form. The anion exchange resins pass into the sulfate form during the oxidation of sulfites (reaction 6), so during regeneration, sulfates are exchanged for sulfites. The main form is interesting in that when using the solutions of bisulfite and sodium metabisulfite, the exchange is accompanied by a neutralization reaction, which generally shifts the balance of the process towards the conversion of the anion exchange resin into the sulfite form (9).



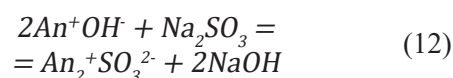
When using sodium metabisulfite in dissolution, the formation of sodium bisulfite occurs (reaction 10), and then the process follows the reaction (9).



It should be noted that under these conditions, the exchange reaction with the formation of alkali is less likely (11).

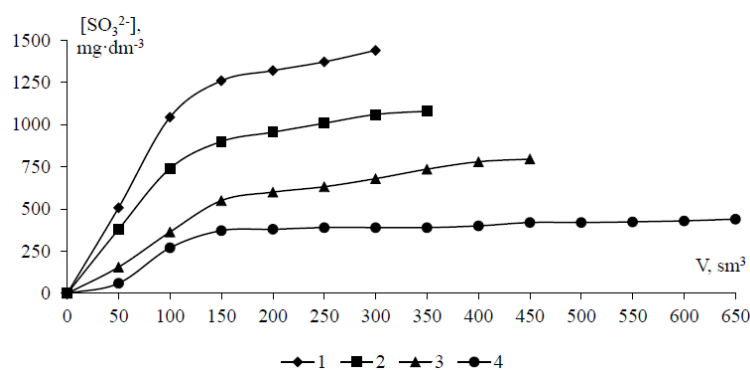


However, in this case, the alkali will bind with metabisulfite to form sodium sulfite, which will prevent alkalization of the aquatic environment. However, in the case of sodium sulfite, the use of anion exchange resin in the main form is undesirable, as the process will be slowed down by alkalizing the regeneration solution. (12).



At the first stage of research the dependence of the capacity of the AB-17-8 anion exchange resin in Cl – form on the concentration of solutions of sodium sulfite was studied (Fig. 5). As can be seen from Figure 5, the capacity of the anion exchange resin strongly depends on the initial concentration of sodium sulfite. In this case, the sorption data shows that up to a concentration of sodium sulfite of 8%, the exchange follows the usual scheme described by equation 5. Only at a concentration of sodium sulfite of 10%, the above-equivalent sorption of sulfite anions is partially realized (reaction 8).

Unexpectedly high result on the sorption capacity of the AB-17-8 anion exchange resin in sulfate form was obtained during its treatment with a 10% solution of sodium sulfite (Fig. 6). In this case, the total dynamic exchange capacity is much higher, as in the case of using the AB-17-8



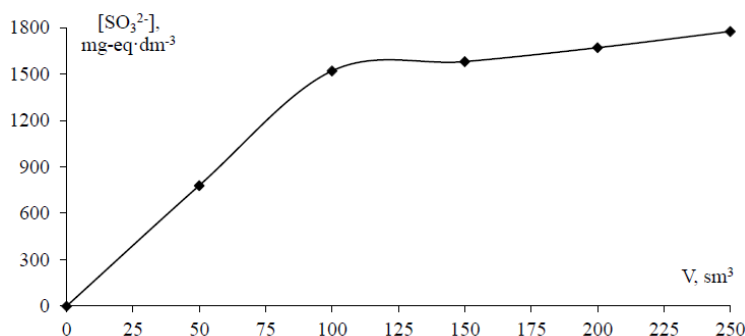
**Figure 5.** Dependence of the sulfite anions concentration in solutions of sodium sulfite concentrations, %: 3 (4), 6 (3), 8 (2), 10 (1), on the volume passed through the AB-17-8 anion exchange resin ( $V_i=50 \text{ sm}^3$ ) (FEDC,  $\text{mg}\cdot\text{eq}\cdot\text{dm}^{-3}$ : 2416 (1), 1884 (2), 1550 (3), 930 (4))

anion exchange resin in chloride form (Fig. 5). It is known that the selectivity of this resin is higher for sulfates than for chlorides. However, at high reagent concentrations, the level of concentrations plays a major role, rather than the selectivity of the resin. Thus, the resin is converted into the desired shape during regeneration. In addition, when converting the anion exchange resin to the sulfite form from the chloride form (Fig. 5) 50 cm<sup>3</sup> of the resin was treated with 300 cm<sup>3</sup> of 10% Na<sub>2</sub>SO<sub>3</sub> solution, and when using the AB-17-8 anion exchange resin in the sulfate form (Fig. 6), only 20 cm<sup>3</sup> of ion exchanger was treated with 250 cm<sup>3</sup> of 10 % sodium sulfite solution. That is, in the first case, the consumption of regeneration solution was 6 volumes per 1 volume of resin, whereas in the second case, the consumption of regeneration solution was 12.5 volumes per 1 volume of resin. Obviously, this contributed to the fact that the regeneration process took place according to the scheme of over-equivalent sorption (reaction 8), while when using an excess of 6: 1 solution (Fig. 5), reaction 8 was realized only partially.

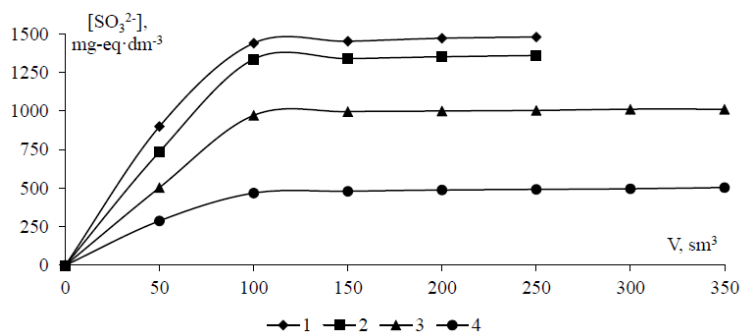
Subsequently, taking into account the ease of conversion of low-basic anion exchangers into the basic form, studies were conducted with low-basic anion exchangers, such as: Dowex Marathon WBA and AMBERLITE IRA 96. Anion exchangers were used in chloride and basic form. Sulfite sorption curves on the Dowex Marathon WBA anion exchange resin are presented in Figure 7.

The following initial concentrations of sodium sulfite solutions were used: 10%, 8%, 6% and 3%. FEDC accordingly made: 1545 mg·eq·dm<sup>-3</sup>, 1890 mg·eq·dm<sup>-3</sup>, 1225 mg·eq·dm<sup>-3</sup> and 1025 mg·eq·dm<sup>-3</sup>. The sorption capacity of the anion exchange resin AMBERLITE IRA 96 can be assessed by the results shown in Figure 8.

The sorption of sulfite anions on AMBERLITE IRA 96 anion exchange resin in Cl – form was performed from the Na<sub>2</sub>SO<sub>3</sub> solutions with concentrations: 10%, 8%, 6% and 3%. The AMBERLITE IRA 96 anion exchange resin is close to the Dowex Marathon POD and is: 1640 mg·eq·dm<sup>-3</sup>, mg·eq·dm<sup>-3</sup>, 1460 mg·eq·dm<sup>-3</sup>



**Figure 6.** Dependence of the concentration of sulfite anions in a solution of sodium sulfite concentration of 10 % when filtering it through the AB-17-8 anion exchange resin (V<sub>i</sub>=20 sm<sup>3</sup>) in salt SO<sub>4</sub><sup>2-</sup>-form (FEDC=4238 mg·eq·dm<sup>-3</sup>)

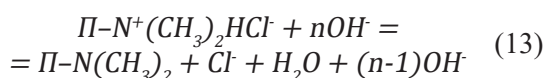


**Figure 7.** Dependence of the concentration of sulfites (1, 2, 3, 4) on the volume of solutions of sodium sulfite through the Dowex Marathon WBA anion exchange resin in Cl<sup>-</sup>-form (V<sub>i</sub>=20 sm<sup>3</sup>) concentrations, %: 3 (4), 6 (3), 8 (2), 10 (1) (FEDC mg·eq·dm<sup>-3</sup>: 1545 (1), 1890 (2), 1225 (3), 1025 (4))



and 780 mg-eq·dm<sup>-3</sup>, respectively, depending on the concentration of the Na<sub>2</sub>SO<sub>3</sub> solution.

As can be seen from Figures 7 and 8, weakly-basic anion exchange resins in chloride form have a rather low capacity for sulfite anions. This is due to the fact that these anion exchangers, regardless of the concentration of sodium sulfite, are able to sorb sulfite anions only by the scheme of equivalent ion exchange. At the same time, their sorption capacity decreases with the slightest increase in the pH of the medium due to the transition from the ionic to associated form which is inactive for the exchange of any ions.

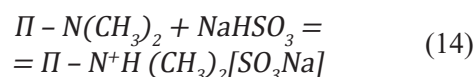


where:  $\Pi$  – the remainder of the polymer matrix of the anion exchange resin.

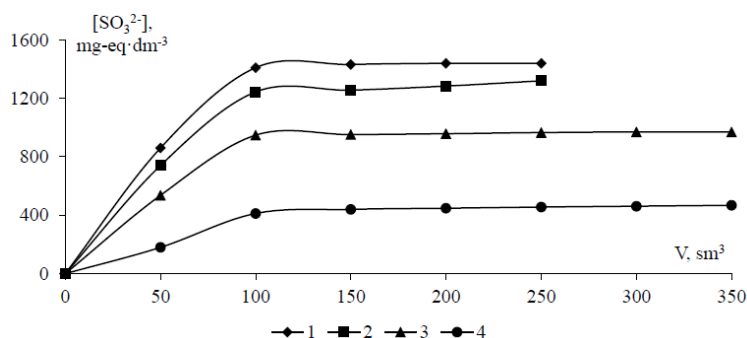
On the other hand, this property of weakly-basic anion exchangers is their advantage, due to the ease of converting them from salt to the basic form by reaction 13. In this case, it is interesting

to use these anion exchangers in the basic form for sorption of sulfite anions. The results of sorption of sulfite anions from a solution of sodium bisulfite on the AMBERLITE IRA 96 anion exchange resin in the main form are shown in Figure 9.

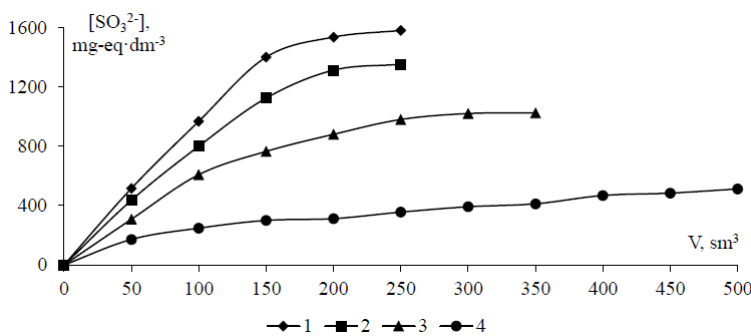
As can be seen from Figure 9, the capacity of weakly-basic anion exchange resin in the basic form of sulfite anions from sodium bisulfite solution is 2 and more times higher than their capacity in chloride form during sorption of sulfite anions from sodium sulfite solution. It is obvious that in this case, the main contribution is the ability of low-base anion exchangers to salt formation in weakly acidic solutions while providing superequivalent sorption of sulfite anions.



At the same time, at concentrations of sodium bisulfite of 3–10%, the total exchange capacity of the anion exchange resin for SO<sub>3</sub><sup>2-</sup> anions reaches 3660–4790 mg-eq·dm<sup>-3</sup>. That is, at



**Figure 8.** Dependence of the concentration of sulfites (1, 2, 3, 4) on the volume of sodium sulfite passed through the AMBERLITE IRA 96 anion exchange resin in Cl-form ( $V_i=20$  sm<sup>3</sup>) concentrations, %: 3 (4), 6 (3), 8 (2), 10 (1) (FEDC mg-eq·dm<sup>-3</sup>: 1640 (1), 1690 (2), 1460 (3), 780 (4))



**Figure 9.** Dependence of the initial concentration of sulfites (1, 2, 3, 4) on the volume of sodium bisulfite solution passed through the AMBERLITE IRA 96 anion exchange resin in OH-form ( $V_i=20$  sm<sup>3</sup>) concentrations, %: 3 (4), 6 (3), 8 (2), 10 (1) (FEDC mg-eq·dm<sup>-3</sup>: 4790 (1), 4340 (2), 4240 (3), 3660 (4))

3% concentration of sodium bisulfite, there is an equivalent sorption. For comparison, at a concentration of sodium sulfite of 3% (Fig. 8), the capacity of this anion exchange resin on sulfite anions reached only  $780 \text{ mg}\cdot\text{eq}\cdot\text{dm}^{-3}$ .

Therefore, it can be said that in the one-stage regeneration of redoxite based on anion exchange resins with sodium sulfite, weakly-basic anion exchangers are unpromising due to the low capacity of sulfite anions. However, in the two-stage regeneration, which involves the conversion of the anion exchange resin into the main form with its subsequent treatment in the second stage with sodium bisulfite, the use of these anion exchange resins is quite appropriate, as it provides a high level of redox.

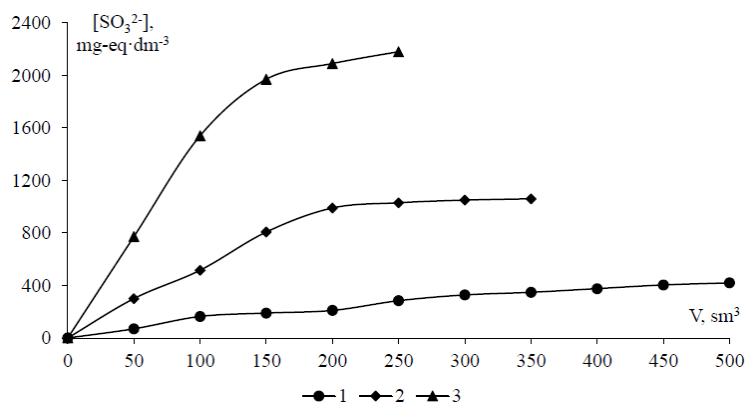
In previous studies, the effectiveness of the AB-17-8 anion exchange resin in sulfite form for water deoxidation was studied. The anion exchange resin was converted to the sulfite form with sodium sulfite. However, it is known that sodium metabisulfite is a cheap and affordable reagent compared to sodium sulfite. Therefore, a series of experiments were performed to determine the sorption capacity of the AB-17-8 anion exchange resin in salt and basic forms for sulfite anions during sorption from solutions of sodium metabisulfite. The results of sorption of sulfite anions on the AB-17-8 anion exchange resin are shown in Figures 10–13.

As can be seen from Figures 10–13, the anion exchange resin in this case is characterized by superequivalent sorption of sulfite anions, regardless of the form of the anion exchange resin. The sorption capacity increases along with the concentration of sodium metabisulfite from 2 to 10%. At the lowest concentration of

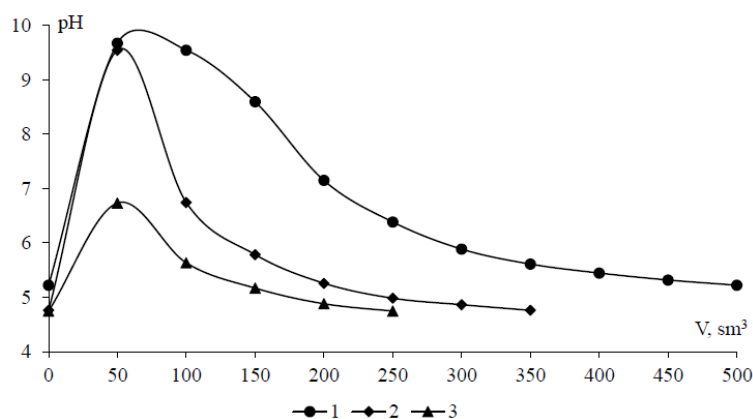
sodium metabisulfite (2%), the capacity of the anion exchange resin reaches  $3500\text{--}3600 \text{ mg}\cdot\text{eq}\cdot\text{dm}^{-3}$ . This capacity can also be explained by the equivalent sorption of  $[\text{SO}_3\text{Na}]$  ions. However, when the concentration of sodium metabisulfite increases to 5% and 10%, the exchange capacity of the anion exchange resin reaches  $4000 \text{ mg}\cdot\text{eq}\cdot\text{dm}^{-3}$  (with 5% solutions) and  $5800$  and  $6700 \text{ mg}\cdot\text{eq}\cdot\text{dm}^{-3}$  for 10% solutions (larger the value of the exchange capacity for the anion exchange resin in the basic form). Such a high capacity of the anion exchange resin over sulfites simply cannot be explained by sorption of the anion  $[\text{SO}_3\text{Na}]$ . It is obvious that the sorption of anions of the  $[\text{NaS}_2\text{O}_5^-]$  type is quite possible in concentrated solutions, especially from the last samples of regeneration solution, the concentration of which is close to 10%, and the pH is 4.70–4.80.

Usually, a certain part of sulfite anions can collect in the pores of the anion exchange resin without ion exchange processes. In order to determine this effect, the anion exchangers after sorption were washed with distilled water. The results are shown in Figures 14 and 15.

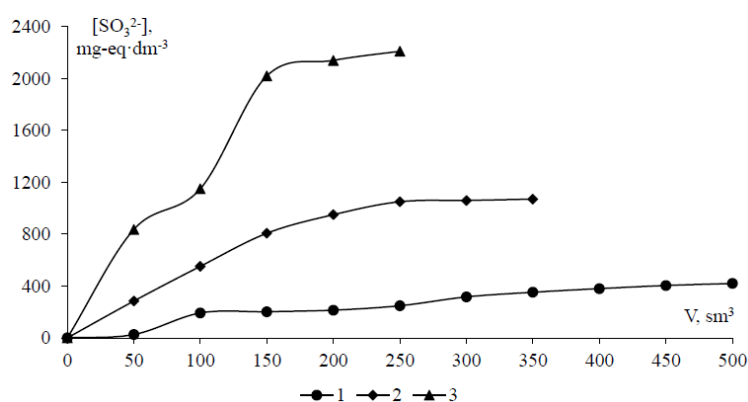
As can be seen from Figures 14 and 15, the concentration of sulfites in the wash water was higher the higher it was in the regeneration solutions. Most likely, the ions were washed away together with the regeneration solution in the pores. However, the capacity of the sorbent was determined by the change in the concentration of sulfites in the solutions that passed through the resin. Therefore, in general, this does not exclude the possibility of sorption of anion exchange resins  $[\text{NaS}_2\text{O}_5^-]$  when using sodium metabisulfite.



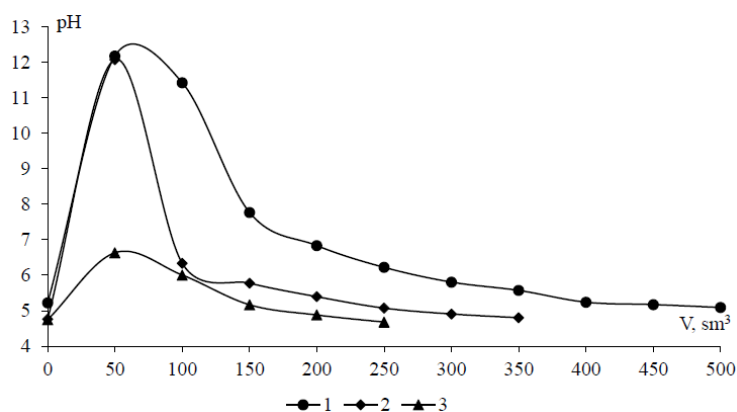
**Figure 10.** Dependence of sulfite anions concentration in the medium (1; 2; 3) on the passed volume of sodium metabisulfite solution concentration, %: 2 (1); 5 (2); 10 (3) through the AB-17-8 anion exchange resin in  $\text{Cl}^-$ -form ( $V_i=20 \text{ sm}^3$ ) ( $\text{FEDC}_1=3515 \text{ mg}\cdot\text{eq}\cdot\text{dm}^{-3}$ ;  $\text{FEDC}_2=4167 \text{ mg}\cdot\text{eq}\cdot\text{dm}^{-3}$ ;  $\text{FEDC}_3=5870 \text{ mg}\cdot\text{eq}\cdot\text{dm}^{-3}$ )



**Figure 11.** Dependence of pH of the medium (1; 2; 3) on the passed volume of sodium metabisulfite solution concentration, %: 2 (1); 5 (2); 10 (3) through the AB-17-8 anion exchange resin in Cl<sup>-</sup>-form ( $V_i=20 \text{ sm}^3$ )



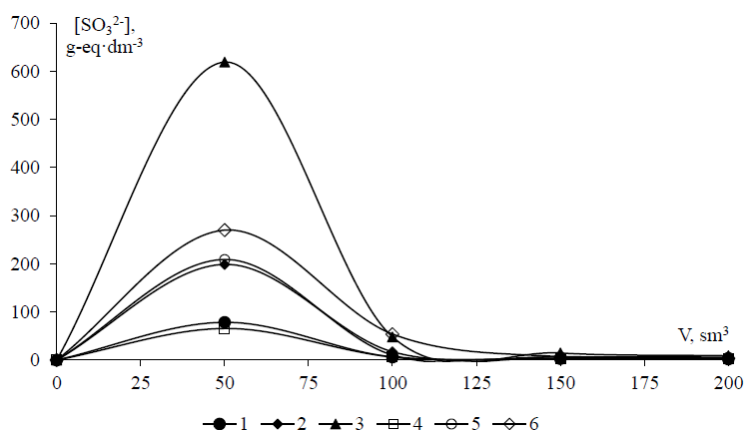
**Figure 12.** Dependence of the concentration of sulfite anions (1; 2; 3) on the passed volume of sodium metabisulfite solution concentration, %: 2 (1); 5 (2); 10 (3), through the AB-17-8 anion exchange resin in the basic form ( $V_i=20 \text{ sm}^3$ ) ( $\text{FEDC}_1=3615 \text{ mg-eq}\cdot\text{dm}^{-3}$ ;  $\text{FEDC}_2=4293 \text{ mg-eq}\cdot\text{dm}^{-3}$ ;  $\text{FEDC}_3= 6735 \text{ mg-eq}\cdot\text{dm}^{-3}$ )



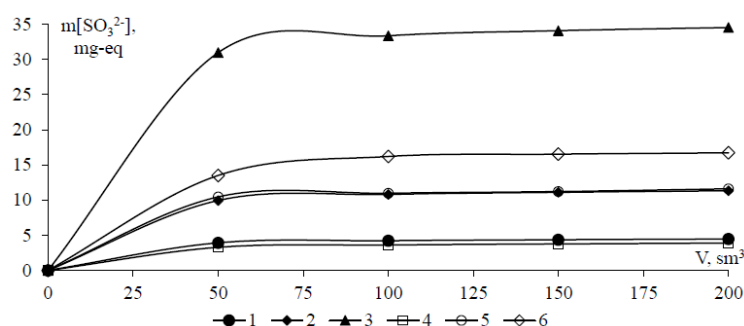
**Figure 13.** Dependence of pH of the medium (1; 2; 3) on the passed volume of sodium metabisulfite solution concentration, %: 2 (1); 5 (2); 10 (3) through the AB-17-8 anion exchange resin in the basic form ( $V_i=20 \text{ sm}^3$ )

In order to assess the real regenerative capacity of the anion exchange resin, various samples of it, with a volume of  $20 \text{ cm}^3$ , were filled with a solution of iodine of a fixed concentration. The solution was stirred for 24 hours and then titrated with excess iodine. Table 3 shows

the results of titration and calculations. Table 3 shows that in all cases, high values of the regenerative capacity of the modified anion exchangers were observed. The values are close to the obtained values of the total exchange capacity for sulfite anions.



**Figure 14.** Dependence of the sulfite anions concentration (1; 2; 3; 4; 5; 6) AB-17-8 anion exchange resin in sulfite form at the capacity of the resin for  $\text{SO}_3^{2-}$  ions,  $\text{mg}\cdot\text{eq}\cdot\text{dm}^{-3}$ : 3515 (1); 4167 (2); 5870 (3); 3615 (4); 4293 (5); 6735 (6)



**Figure 15.** Dependence of the number of washed sulfite ions (1; 2; 3; 4; 5; 6) from the AB-17-8 anion exchange resin in sulfite form at the capacity of the resin ion on  $\text{SO}_3^{2-}$  ions,  $\text{mg}\cdot\text{eq}\cdot\text{dm}^{-3}$ : 3515 (1); 4167 (2); 5870 (3); 3615 (4); 4293 (5); 6735 (6)

**Table 3.** Dependence of RC of AB-17-8 anion exchange resin on its form when modified with sodium metabisulfite, determined iodometrically

Concentration of sodium metabisulfite, %	Ability to reduce $\text{I}_2$ , $\text{mg}\cdot\text{eq}\cdot\text{dm}^{-3}$	
	Form of anion exchange resin AB-17-8	
	$\text{Cl}^-$	$\text{OH}^-$
2	3274	3524
5	3898	3918
10	4902	4920

## CONCLUSIONS

The study of redoxites in the  $\text{Fe}^{2+}$ -form and  $\text{Na}^+$ -form modified with  $\text{Fe}(\text{OH})_2$  in water deoxidation processes and their advantages and disadvantages. It was shown that the modified cation exchange resins, i.e. KU-2-8 and Dowex Mac-3 in the  $\text{Fe}^{2+}$ -form, are characterized by a high reducing ability ( $\text{RC} = 1600 \text{ mg}\cdot\text{eq}\cdot\text{dm}^{-3}$ ).

It was shown that the sorption of sulfite anions on highly basic anion exchange resins in salt form depends on the concentration of sodium sulfite solution. It was established that during treatment under dynamic conditions of weakly acidic anion exchangers in salt and basic form with solutions of sulfite and sodium bisulfite, the capacity of sulfites increases along with the concentration of solutions. The sorption capacity of the AB-17-8 anion exchange resin on sulfite anions from sodium metabisulfite solutions was determined. The sorption capacity does not depend on the form of the anion exchange resin, but is determined by the initial concentration of sodium metabisulfite. The reducing ability of the AB-17-8 anion exchange resin depending on its form when modified with sodium metabisulfite was evaluated iodometrically.

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