1. Introduction

Globalization, the rapid development of industry, improvement of cultural and living conditions, as well as several other factors, lead to complicated issues related to environmental pollution. The increased needs by the population and industry for clean water predetermine the interest of states and scientists in finding a solution to this problem. The limited freshwater resources predetermine the relevance of a water purification issue in order to obtain high-quality drinking water for people and technical water for the industry.

The main sources of water reservoirs contamination are the discharge of insufficiently purified wastewater from industrial and communal enterprises. A large source of water pollution is the dumping of significant volumes of water from mines [1]. This leads to the contamination of surface water objects with substances contained in water from mines. Water from mines contains high concentrations of sulfates and hardness ions. Such water bodies are characterized by increased levels of mineralization and hardness. At a concentration of sulfate over 1,000 ppm, there are negative consequences. In addition, the high concentrations of sulfate cause the release of phosphates from sediments, which...
potentially leads to eutrophication [2]. As a result, contaminated surface waters cause environmental and material losses. Consequently, it becomes apparent that mineralized wastewater must be subjected to proper cleaning. Based on the environmental safety requirements, all mineralized waters must be desalinated before being discharged into open water reservoirs.

To implement the environmentally safe industrial water consumption, it is necessary to develop low-waste technology of water desalination. Therefore, it is a relevant task to study the creation of technologies for the comprehensive purification of mineralized water, which would ensure the proper efficiency of water desalination and could process the waste formed, with obtaining useful products.

2. Literature review and problem statement

To reduce the shortage of freshwater and to reduce anthropogenic pressure on the environment, it is necessary to implement appropriate technologies for the purification of mineralized waters. There are many methods to purify mineralized wastewater, which include reagents-based, ion-exchange, membrane, electrochemical, biological, and others. The authors of [3] compared different methods to purify water from sulfates. It is shown that in the purification of water with the original concentration of sulfates 1,400, 700, 350, and 20 mg/dm³, the most effective was the reverse osmosis.

Paper [4] investigates the application of ultrafiltration, nanofiltration, reverse osmosis, membrane distillation, and integrated membrane processes to produce technological water from natural waters or industrial drains. It is shown that at prolonged filtering there is the formation of salt deposits. This leads to a decrease in the service life of membranes and increases the cost of the cleaning process.

The authors of work [5] applied, for the treatment of water from mines, the nano-filtering, and inverse osmotic membranes, and the efficiency of sulfate extraction was 97 % and 99 %, respectively. The efficacy of the extraction of copper, aluminum, iron, and manganese for both membranes did not exceed 95 %.

Work [6] reported a designed membrane that has potential use in the coal industry for the reuse of water, the processing of tails, pre-treatment of water before reverse osmosis.

It is shown in [7] that the application of pre-filtering at nanofiltration and reverse osmosis is appropriate from an environmental and economic point of view. The efficiency of the nanofiltration process is 90 % and 95 % for NaCl and Na₂SO₄, respectively.

The high price, the necessity to develop methods of brine processing, preliminary processing of solutions before feeding to membranes are the main issues for achieving the efficient cleaning of water from mines [8].

Thus, membrane technologies have a significant disadvantage [3–8]. The result of reverse osmotic treatment is the large volumes of concentrates, characterized by the elevated concentration of sulfates and hardness ions.

The concentration of dissolved solids in brine is from 20,000 to 35,000 mg/dm³, so it is quite expensive to process it and dispose of it [9].

To recycle the concentrates from baromembrane purification, it is proposed to use the biological reduction of sulfate to sulfur [3]. The main disadvantage of a given method is the high sensitivity of biological methods. In addition, at the desalination of mineralized waters, the concentrate, in addition to sulfates, contains a considerable amount of hardness ions.

Paper [10] uses lime to clean and soften water. A given method is quite simple and cheap. However, this method of wastewater treatment does not make it possible to reduce the sulfate concentration by less than 1,500 mg/dm³, due to the solubility of gypsum, at a sanitary norm of 250–500 mg/dm³ for drinking water and >100 mg/dm³ for fish farms.

Article [11] investigates the processes of water purification by sulfates when processing with lime, sodium aluminate. The disadvantage of sodium aluminate is the large values of residual water alkalinity. In addition, to align the pH of solutions, they must be treated with carbon dioxide.

Comprehensive technology for the purification of mineralized water was offered in paper [12]. Cleaning the baromembrane desalination concentrates was carried out by treating samples with lime and 2/3 of aluminum hydroxochloride. The paper shows that at a dose of coagulant 7.82 mmol/dm³ and consumption of lime of 134.0 mg-eq./dm³, it was possible to reduce sulfate concentration to 2.7 mg-equiv./dm³. The residual alkalinity of water increases with an increased lime consumption but decreases while increasing the dose of the coagulant, which contributes to water acidification. The main drawback of a given process is significant secondary contamination of water by chlorides.

Mineralization of coal-mining waters varies from 1–3 to 20–30 g/dm³. Therefore, our research is aimed at the desalination of weakly and highly mineralized waters for obtaining drinking water for people or technical water for the needs of the industry. The research also aims to resolve a complex unresolved issue – the disposal of the concentrates with a high chloride content.

3. The aim and objectives of the study

The aim of this study is to create a technology to treat wastewater from mines, with varying levels of mineralization, to produce freshwater for people and industrial enterprises, taking into consideration the issues related to processing the formed salt solutions into target products.

To accomplish the aim, the following tasks have been set:
- to determine conditions for the ion-exchange softening of water with different levels of mineralization to improve the efficiency of water baromembrane desalination process and prolong the service time of membranes;
- to assess the effects of mineral salt concentration in solutions on the effectiveness of their desalination depending on the solution characteristics;
- to define parameters for processing the baromembrane water purification concentrates while obtaining useful products.

4. Methods for estimating the baromembrane and reagent purification of mineralized water

To desalinate mineralized water from mines, we used the nano-filtration membrane OPMN-P and the reverse osmosis low-pressure membrane Filmtec TW30-1812-50. To determine the process efficiency, we used a low-mineralized solution, close in composition to water, from the city of Torrets: (SO₄²⁻)=15.0 mg-equiv./dm³, H⁺=10.3 mg-equiv./dm³, A⁻=4.6 mg-equiv./dm³, C(Cl⁻)=3.1 mg-equiv./dm³, pH=
~8.47. And a highly mineralized solution (from the mine Kreminna, Donetsk oblast): $C_{(SO_4^2-)}=32.0$ mg-equiv./dm$^3$, $H^+=58.9$ mg-equiv./dm$^3$, $A=18.7$ mg-equiv./dm$^3$, $C_{(Cl^-)}=\sim 500.0$ mg-equiv./dm$^3$, pH=6.53. Concentrated solutions containing NaCl in concentrations over 30 % are practically not softened on strong acidic cations. Therefore, for the stabilizing treatment of water relative to the carbonate deposits, the ion exchange softening of this solution was used based on the weakly acidic cation exchanger DOWEX MAC-3 in the H$^+$ and Na$^+$ forms. After that, the filtrate was fed to the baromembrane purification.

The solution was poured into a cell of 1.0 dm$^3$ with a membrane area of 113.04 cm$^2$ at nanofiltration desalination. The operating pressure was 0.40 MPa because this pressure provides for sufficiently high process performance. The samples of permeate of 100 cm$^3$ were selected. The degree of permeate selection varied from 10 to 70 %.

At reverse osmosis water desalination, we poured a solution of 10 dm$^3$. The operating pressure was 0.40 MPa. The stopwatch registered the time of selecting 1 dm$^3$ of the permeate. The degree of permeate selection varied from 10 to 70 % for strongly-and 90 % for weakly mineralized water.

In the permeate, we determined the content of sulfates, chlorides, hardness, alkalinity, and a pH of the medium. We calculated the selectivity and performance of the nano-filtering and reverse-osmotic membrane [12].

In order to soften and clean the concentrates after water membrane desalination, the reagent methods were used. The reagents used were lime, sodium hydroxaluminate, aluminum hydroxochloride, synthesized in a laboratory. When stirring, water was treated with reagents, aged at 40 °C in a thermostat for 2 hours. Sediment was separated on a paper filter “Blue Ribbon”; in the filtrate, we determined hardness, alkalinity, the concentration of sulfates, chlorides, and a pH of the water. The formed sediment was separated on the filter, analyzing the solution for all the above indicators. The degree of softening ($Z_1$) and the degree of sulfate extraction from water ($A$) were calculated from formulae given in [13].

5. Results of studying the purification of mineralized water

5. 1. The efficiency of water softening using DOWEX MAC-3 depending on the form of an ionite and the composition of a solution

The effectiveness of the baromembrane desalination of water and the service time of membranes depends on the quality of their pre-purification. The high- and low-mineralized solutions were passed through DOWEX MAC-3 in the H$^+$ and Na$^+$ forms. The cation exchanger DOWEX MAC-3 has a high capacity for hardness ions, both in cleaning the low-mineralized solutions (Fig. 1) and in the purification of highly mineralized solutions (Fig. 2, 3).

The weakly acidic cation exchanger DOWEX MAC-3 in the H$^+$ and Na$^+$ forms does not sorbate the cations of metals from the solutions of salts of strong acids. In cases where solutions demonstrate hydrocarbonate alkalinity, there is the decarbonization of water and its softening. This leads to water acidification and a decrease in its pH to ~4. When the cation exchange capacity is depleted, the pH increases to 7.3 and the alkalinity to 17–18 (Fig. 2). Thus, a given method could be effectively used for the treatment of low mineralized waters.

At the sodium-cation softening of water, the hardness ions change for the ions of sodium, so the hydro carbonates of magnesium and calcium are transferred to sodium bicarbonate. Alkali is a much stronger substrate than the calcium and magnesium hydroxides, so the hydrolysis of sodium bicarbonate is stronger. Therefore, when one passed a highly mineralized solution through the ionite DOWEX MAC-3 in the H$^+$ and Na$^+$ forms, there is an increase in pH to 7.5–8.9. The capacity of the weakly acidic cation exchanger for hardness ions is quite high, independent of the concentration of sodium ions in the solution. At the concentration of sodium
chloride of $\sim 29$ g/dm$^3$, full exchange dynamic capacity for hardness ions in the cation exchanger DOWEX MAC-3 reaches 3,000 mg-equiv./dm$^3$. Thus, DOWEX MAC-3 makes it possible to soften water effectively in order to ensure the stabilizing treatment of water before its baromembrane desalination.

5.2. The effectiveness of baromembrane desalination depending on the characteristics of a solution

The performance of the nano-filtration membrane decreases with an increasing degree of permeate selection, which is primarily due to the growth of salt content in the concentrate and the increase of osmotic pressure [12]. When filtering a low-mineralized solution at a working pressure of 0.4 MPa, we observed a decrease in performance from 8.17 to 6.80 dm$^3$/m$^2$·h, that is, by dm$^3$/m$^2$·h. When filtering a cationic solution, this indicator decreased from 8.85 to 7.69, that is, by 1.16 dm$^3$/m$^2$·h. The filtering time of the non-cation model solution was short enough for the formation of significant deposits on its surface. At prolonged filtering of the non-treated solution, the membrane performance would significantly decrease.

The selectivity of the membrane for sulfates when filtering a model solution was within 92.3–93.3 %, for the ions of hardness – 85.4–90.5 %. For the filtered solution, the selectivity of the membrane for chlorides is zero, similar to that of the non-treated solution, for sulfates, it is 73.9–77.9 %, for hardness ions – 64.9–70.5 %, which is 16–24 % lower compared to the non-treated solution. Thus, after treating the solution on cation exchanger DOWEX MAC-3, we observed a slight reduction in the selectivity of the OPMN-P membrane. This is due to that the lowering of the pH changed the state of the hydrate shells of double-charged ions, sulfate anions, and cations of hardness. Water acidification influences the value of the electro-kinetic potential of the membrane surface and leads to the destruction of the hydrate membrane at the membrane surface and at the surface of the membrane’s pores [12].

The desalination of the solution was accompanied by an increase in the content of sulfates in the concentrate of up to 32.6 mg-equiv./dm$^3$ at a hardness of 28.5 mg-equiv./dm$^3$, alkalinity 4.35 mg-equiv./dm$^3$, the chloride content, similarly to the original solution, was 3.1 mg-equiv./dm$^3$. In an acidic solution, the content of sulfates and hardness ions are smaller, which is associated with the lower selectivity of the membrane for these pollutants. Thus, at the nano-filtering purification of weakly mineralized waters, their desalination occurs due to the extraction of sulfates and partial water softening; chlorides and hydro carbonates are not retained.

Therefore, the nano-filtering water desalination is appropriate for low-mineralized waters with acceptable chloride content. At the desalination of highly mineralized concentrate, it is advisable to use reverse osmosis. The performance of the membrane at a working pressure of 0.40 MPa practically does not depend on the method for the preliminary stabilizing treatment of the solution because the filtration of small volumes of water produces almost no sediments on the membrane. At the filtration of large volumes of water, membrane performance at the stabilizing treatment of water would remain quite high for a long time of use. Acidification of solutions, extraction of hydrocarbons from them with partial softening provides stable operation of reverse osmosis membranes.

In the acidic weakly- and strongly mineralized solutions, the selectivity of the membrane for sulfates and hardness ions is more than 99 %, regardless of the reaction of the medium and the degree of permeate selection. In this case, the decrease in the selectivity for chlorides is observed (Fig. 4).

At the maximum degree of permeate selection from weakly mineralized water, the content of sulfates in the concentrates reaches ~70 mg-equiv./dm$^3$, hardness ions ~50 mg-equiv./dm$^3$, chlorides ~12 mg-equiv./dm$^3$. At the desalination of strongly mineralized water, the content of sulfates in the concentrates reaches ~90 mg-equiv./dm$^3$, hardness ions ~150 mg-equiv./dm$^3$, chlorides ~1,500 mg-equiv./dm$^3$.

5.3. Determining the effectiveness of desalinating the concentrates of water baromembrane purification when using aluminum-containing reagents and subsequent disposal of the formed sediments

This work has defined the conditions for the effective softening of solutions and purification from sulfates by the complex treatment of lime and aluminum coagulants based on the conditions of the lowest secondary contamination of water. By choosing a ratio of sodium hydroxaluminate to aluminum hydroxochloride, it is possible to adjust the content of chlorides and sodium ions in the purified water. In this case, there occurred the neutralization of the alkali formed in the hydrolysis of sodium hydroxaluminate with hydrochloric acid, which was formed in the hydrolysis of aluminum hydroxochloride. Therefore, it is not necessary to use carbon dioxide to reduce the pH of the medium, which greatly simplifies the process. In addition, it is possible to achieve a high degree of water softening and sulfate removal.

Using lime can reduce sulfate concentration to 30 mg-equiv./dm$^3$, so in further studies, this concentration was taken as original. The softening of the baromembrane water purification concentrate was quite effective. The efficiency of softening increased with reducing the consumption of lime, while increasing the dosage of CaO decreased the residual sulfate concentration. At the reagent softening of the concentrate formed during the baromembrane desalination of a highly- and low-mineralized solution, the alkalinity was within admissible limits (Fig. 5, 6). The total mineralization decreased to permissible values (>1,000 mg/dm$^3$). Such water can be discharged to sewage or re-used at water treatment.
The formed sediment can be added to cement in quantities 2.5, 5.0, and 7.5\% by weight \[14\]. Thus, up to 7.5\% by weight of cement can be replaced with the sediment formed during reagent water purification, without deteriorating the physical and mechanical parameters of the material.

6. Discussion of results of the desalination of mineralized waters and the development of a technological scheme for the comprehensive purification of water from mines

One variant to implement the developed processes is a fundamental technological scheme of the comprehensive purification of water from mines, wastewater, and concentrates during the complete processing of waste which is formed (Fig. 7). After a wastewater averager (1), mineralized water enters the ultrafiltration membrane (3) for purification from suspended substances. This makes it possible to reduce the load on a reverse osmosis membrane, increase the productivity of the process with a decrease in energy costs, prolong the service life of the membranes. The stabilizing treatment of water, in terms of carbonate deposits and preventing the fouling on membranes that leads to a decrease in the flow of the filtrate and an increase in osmotic pressure, employs the ion exchange water softening using the weakly acidic cation exchanger Dowex MAS-3 in an acidic or salt form (5). If the original solution contains a low concentration of chlorides, it is advisable to desalinate it on a nanofiltration membrane (6), which completely retains sulfates and ions of hardness and passes chlorides. To desalinate highly mineralized waters, it is advisable to use reverse osmosis. Concentrates with a high content of sulfates and hardness ions should be purified by depositing sulfates and by softening applying reagent methods. For a case of concentrates with a high content of chlorides, they, after reagent softening, should be electrochemically treated to produce active chlorine.

Following the baromembrane purification, concentrates enter a ruff type mixer (14), where lime is portioned, as well as sodium aluminate and aluminum hydroxochloride. This process ensures deep water softening, up to 2.7–1.1 mg-equiv./dm\(^3\). It is possible to reduce the sulfate concentration to 2–3 mg-equiv./dm\(^3\). After the settling tank (15), we obtain softened water along with its clarification and discoloration. The sediment, formed during water desalination, is separated and directed to the processing as an expansion admixture for cement and a sulfate activator for the slag Portland cement.

Applying the proposed technological scheme of the comprehensive treatment of mineralized waters makes it possible to create low-waste technologies for the desalination of these waters, thereby enabling complete processing of the formed liquid and solid wastes into target products.
Water from mines, along with sulfates and chlorides, can contain nitrates. In the use of ion exchange, nitrates can be removed to admissible levels by the desalination of low mineralized waters. The separation of nitrates from highly mineralized waters is a difficult task. Therefore, in further studies, it is necessary to develop environmentally and economically feasible methods to separate these anions, which would make it possible to effectively desalinate water and recycle the wastes with obtaining target products.

Fig. 7. Principal technological diagram of the comprehensive desalination of wastewater from mines: I – averager of wastewater from mines; II – pumps; III – ultrafiltration membrane; IV – HCl/NaCl consumption tank; V – cation exchanger filter Dowex MAC-3; VI – reverse osmotic/nanofiltration membrane; VII – receiving chamber; VIII, IX, X – solution containers for lime, sodium aluminate, aluminum hydroxochloride; XI, XII, XIII – discharge containers for lime, sodium aluminate, aluminum hydroxochloride; XIV – ruff type mixer; XV – vertical vortex settler; XVI – sludge storage device; XVII – MgCO₃ discharge tank; XVIII – regenerative solution reservoir; I – supply of wastewater from mines; II – water to consumer; III – return of water after the settler to the averager; V – discharge to urban sewage; IV, VI – MgCl₂ for evaporation and drying; VII – sediment for processing in building materials; VII – supply of solution to electrolysis

Most water resources have an elevated level of mineralization, so they require effective comprehensive preparation. Our technologies for the desalination of low- and highly mineralized waters make it possible to obtain water of the required quality to ensure the needs of industry and people.

7. Conclusions

1. We have developed methods of the stabilizing treatment of low- and highly mineralized waters in the processes of their baromembrane desalination in order to improve the efficiency and service time of the membranes. It has been shown that the weakly acidic cation exchanger Dowex MAC-3 ensures the effective extraction of hardness ions from low-mineralized water and water with a concentration of NaCl up to 10 %. It has been demonstrated that the nanofiltration membrane OPMN-P provides for the effective purification of low mineralized waters from sulfates and hardness ions. The membrane does not retain chlorides at the low selectivity for bicarbonate anions. This avoids accumulating these anions in the concentrates at the nanofiltration water purification.

2. It has been established that it is advisable to use the reverse osmosis membrane Filmtec TW30-1812-50 for the desalination of highly mineralized waters. The selectivity of the membrane for sulfates and hardness ions is ~99 % for waters of different chemical composition. The selectivity of low mineralized waters for chlorides is more than 90 % in a non-treated solution and 75–83 % in the acidic solution, highly mineralized – 90 % and 95 %, respectively.

3. We have developed ways to process the concentrates of baromembrane water purification in order to create the low-waste technologies of water demineralization. It has been shown that at the ratio of sodium hydroxaluminate to aluminum hydroxochloride 1:1, it was possible to effectively desalinate the low- and highly mineralized water concentrates. For the case of desalinating the concentrate of low mineralized waters, the sulfate concentration decreased to 2.55–6.53 mg-equiv./dm³ and hardness ions – to 3.31–9.02 mg-equiv./dm³. The sulfate concentration decreased to 3.71–8.23 mg-equiv./dm³ and hardness ions – to 4.20–10.65 mg-equiv./dm³ in the concentrate after the reverse osmotic desalination of highly mineralized waters. We have developed a technological scheme of the comprehensive treatment of mineralized waters, which enables the creation of the low-waste technologies for the desalination of these waters with the complete processing of sediments that are formed.

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