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DEVELOPMENT OF A RESOURCE-SAVING TECHNOLOGY FOR INTEGRATED PROCESSING OF HIGHLY MINERALIZED MINE WATER IN THE ENTERPRISES OF THE KRYVYI RIH IRON ORE BASIN

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In terms of the intensity, scale and negative consequences of the impact on the ecological state of the hydrological system of the Kryvyi Rih iron ore basin, the leading place belongs to enterprises and facilities of the mining industry. First of all, the discharge of untreated or insufficiently treated wastewater from industrial enterprises has a significant impact. Under such conditions, the surface waters of the Ingulets and Saksagan Rivers, within the limits of the Kryvyi Rih iron ore basin, have practically lost their natural properties. Firstly, their hydrological regime has changed, and secondly, the salt and microcomponent composition has undergone significant changes. An analysis of the existing desalination methods showed that not all methods are suitable for the demineralization of mine waters with a high salt content and / or with a large volume of mine waters, as in the case of Kryvyi Rih. A resource-saving technology for the complex processing of highly mineralized mine waters by mining enterprises of the Kryvyi Rih iron ore basin has been developed. Of all the known methods of water desalination, the only potentially technically and economically feasible method in this case is reverse osmosis in combination with evaporation and crystallization. The proposed processing technology is based on the successive application of several stages, namely: pre-treatment of polluted mine waters by coagulation and soda-lime softening; desalting at a reverse osmosis plant; evaporation of the reverse osmosis concentrate in an evaporator with further evaporation of the salt concentrate in a vacuum crystallizer; dehydration of salt sludge in a centrifuge with additional drying of salt crystals in a rotary disk dryer. The introduction of the proposed technology makes it possible to obtain demineralized water, the hydrochemical parameters of which correspond to the quality standards of surface water bodies, and marketable mineral products that can be used as valuable raw materials for the needs of the national economy. *Key words:* mining enterprises, highly mineralized mine waters, water desalination methods, resource-saving technology, water quality standards.

Розробка ресурсозберігаючої технології комплексної переробки високомінералізованих шахтних вод підприємств Криворізького залізорудного басейну. Кулікова Д.В.
За інтенсивністю, масштабами й негативними наслідками впливів на екологічний стан гідрологічної системи Криворізького залізорудного басейну провідне місце належить підприємствам і об'єктам гірничодобувної галузі. Перш за все, суттєво впливає скид неочищених або недостатньо очищених стічних вод промислових підприємств. За таких умов поверхневі води річок Інгулець та Саксагань, в межах Криворізького залізорудного басейну, практично втратили свої природні властивості. По-перше, змінився їхній гідрологічний режим, по-друге, суттєвих змін зазнав сольовий та мікрокомпонентний склад. Аналіз існуючих способів опріснення та знесолення показав, що не всі методи придатні для демінералізації шахтних вод із високим вмістом солей та/чи з великим обсягом шахтних вод, як у випадку Кривого Рогу. Розроблено ресурсозберігаючу технологію комплексної переробки високомінералізованих шахтних вод гірничодобувних підприємств Криворізького залізорудного басейну. З усіх відомих способів знесолення води єдиним потенційно технічно та економічно доцільним методом у цьому випадку є зворотний осмос в поєднанні з випарюванням та кристалізацією. Запропонована технологія переробки основана на послідовному застосуванні декількох стадій, а саме: попередньої обробки забруднених шахтних вод методами коагуляції та содо-вапняного пом'якшення; знесолення на установці зворотного осмосу; випарювання концентрату зворотного осмосу у випарному апараті з подальшим випарюванням сольового концентрату у вакуум-кристалізаторі; зневоднення сольового шламу на центрифузі з досушуванням кристалів солей в роторно-дисковій сушарці. Впровадження запропонованої технології дозволяє отримати знесолену воду, гідрохімічні показники якої відповідають нормативам якості поверхневих водойм, та товарні мінеральні продукти, що можуть використовуватися в якості цінної сировини на потреби народного господарства. *Ключові слова:* гірничодобувні підприємства, високомінералізовані шахтні води, методи знесолення води, ресурсозберігаюча технологія, нормативи якості води.

Formulation of the problem. Mining enterprises have a significant negative impact on water bodies [1, 2]. Its consequence is a constant reduction in reserves and deterioration in the quality of water resources, as a result of pumping and discharging untreated mine and quarry waters into surface water bodies.

In 2020 alone, mining enterprises discharged 191 million m^3 of mine and quarry water into surface water bodies and watercourses of Ukraine [3], most of which is classified as polluted. The most negative impact on surface water bodies is the discharge of a large amount of mineralized mine water.

Research topicality. The aggravation of the shortage of drinking and technical water against the background of increasing technogenic pollution of the environment in a number of mining towns and villages cast doubt on the possibility of further implementation of long-term plans for the development of the mining industry without ensuring environmental safety requirements in terms of the protection and rational use of water resources.

This problem is extremely relevant for the conditions of the Kryvyi Rih iron ore basin, the needs of which in high-quality drinking water are not provided by local sources of water supply, and the degree of degradation of water resources due to excessive pollution by highly mineralized (up to 40 g/dm^3) mine waters with a high chloride content (up to 20 g/dm^3) significantly exceeds similar indicators in other regions [4].

Relation of copyright work with important scientific and practical tasks. Today, mineralized mine waters are of limited use in the industrial water supply of mines and related industries and are mainly discharged into natural reservoirs. In this case, soil salinization and a change in the hydrochemical composition of storage reservoirs occur, which requires additional costs for the elimination of such technogenic consequences. In addition, the discharge of mineralized mine waters has a detrimental effect on the flora and fauna of water bodies.

Until now, among the main technical methods of mine water treatment is their settling in storage ponds with further discharge into water bodies. Additional methods for filtration and reagent water treatment can reduce the content of colloidal substances and iron in it.

The treatment facilities operating at the mining industry enterprises are not designed to remove dissolved mineral salts from mine waters, and the methods and technologies known in world practice to reduce the mineralization of natural and waste water have not been widely used in continental conditions. In connection with the above, the problem of purification (processing) of mineralized mine waters of mining enterprises is quite relevant. Its solution has an important scientific and practical significance.

Analysis of recent research and publications. The existing methods of water desalination are divided into two main groups: with and without changes in its state of aggregation [5-11].

The first group of methods includes distillation, heating water to a supercritical temperature (350 °C), freezing, and the gas hydrate method. The second group of methods includes ion exchange, electrodialysis, reverse osmosis (hyperfiltration), ultrafiltration, extraction, and others.

The oldest methods for obtaining demineralized water (distillate) are thermal methods – distillation and evaporation.

The basis of the process is the transfer of water into the vapor phase with its subsequent condensation. The most important advantage of this method is the minimal amount of reagents used and the volume of waste that can be obtained in the form of solid salts. However, the method also has a number of significant drawbacks. For example, high water consumption, salt deposits on equipment, which makes it difficult to maintain, high energy consumption.

Most often, water desalination is carried out by ion exchange. Until some time, ion exchange was considered the most developed and reliable method of water desalination. The essence of the process is to replace hardness salt ions with sodium ions. By selecting ion exchangers, the degree of their regeneration and the number of purification steps, it is possible to achieve the required depth of water purification of almost any initial composition. The method is good in many respects, but sometimes it is economically unprofitable. In many ways, the choice of this method will depend on the initial indicator for the amount of salts in the water. During desalination by ion exchange, the volume of ion exchangers and equipment, as well as the consumption of reagents, grow in proportion to the salt content of water, that is, capital and operating costs increase. Due to the complexity of operations for the separation of a mixture of ion exchangers and their regeneration, such devices are used mainly for the purification of low-salinity waters. It should be taken into account that salts are found in a small volume of regenerates, respectively, in a high concentration. The direct discharge of such wastes is prohibited, since regenerates, as a rule, have a pH value that is different from the standards, which requires additional costs for their neutralization.

Extraction of dissolved substances from water can be carried out by membrane methods. In this case, the degree of desalination is determined by the membrane selectivity. Usually, when desalination of water, two methods of membrane separation are considered – nanofiltration and reverse osmosis. With nanofiltration, partial desalination of water is achieved. More complete desalination provides high and low pressure reverse osmosis. The total degree of desalination depends on the cationic and anionic composition of water and is approximately 50-70% for nanofiltration, 80-95% for low-pressure reverse osmosis, and 98-99% for high-pressure reverse osmosis. In reverse osmosis, the performance of membrane elements, energy consumption and, accordingly, capital and operating costs are slightly dependent on the salt content. However, during the operation of reverse osmosis plants, an additional source of pollution in the discharges is compounds for chemical washing of reverse osmosis membranes.

Selection of previously unresolved tasks of the general problem. When developing a technological scheme for the treatment of mineralized wastewater, demineralization processes cause the greatest difficulties.

An analysis of the existing methods of water desalination showed that not all methods are suitable for the demineralization of mine waters with a high salt content and/or with such a large volume of mine waters, as in the case of Kryvyi Rih. The choice of desalination method is based on the quality and quantity of water supplied for treatment and the requirements for the quality of purified water, plant capacity, as well as technical and economic aspects. As a rule, to obtain purified wastewater that would meet the requirements of environmental safety [12, 13], it is not enough to use any one method, and therefore, a combination of several physicochemical methods is necessary.

The research novelty lies in the fact that the development of a resource-saving technology for the complex processing of highly mineralized mine waters of the mining enterprises of the Krivoy Rog iron ore basin makes it possible to obtain demineralized water, the hydrochemical parameters of which correspond to the quality standards of surface water bodies, and marketable mineral products that can be used as valuable raw materials for the needs of the national economy.

Methodological or general scientific significance. Compliance with the "Rules for the protection of surface waters from pollution by recycled waters" [14] through the introduction of the proposed technology for the complex processing of highly mineralized mine waters allows the ability of self-purification of water bodies and watercourses to be fully manifested, which leads to the preservation of the purity of water bodies and the sanitary improvement of adjacent territories.

Outline of the main material. The Kryvyi Rih iron ore basin is the largest basin in Ukraine with rich iron ore deposits. It is considered the main mining center of the country, which is located on the territory of the Dnipropetrovsk region.

Recently, the mining enterprises of the Kryvyi Rih iron ore basin annually pump out about 40 million m^3 of wastewater to the surface, among which 21-22 million m^3 of quarry water and 16-17 million m^3 of highly mineralized mine water. Basically, these are waters with a high content of chlorides, sulfates, sodium, potassium, magnesium and calcium ions with an increased level of total mineralization from 5 to 96 g/dm^3. The average value of the total mineralization is 40 g/dm^3 [4].

Approximately 28-30 million m^3 of mine and quarry water per year is used to replenish the circulating water supply systems at mining and processing plants. The rest (10-12 million m^3) of mine water is annually accumulated and temporarily contained in the storage pond located in the Svistunov gully [15, 16].

Periodic discharge of mine water residues from the storage pond leads to a temporary deterioration in the qualitative composition of the surface runoff of the Ingulets River until it is flushed. Firstly, its hydrological regime changes, and secondly, its salt and microcomponent composition changes significantly. The surface waters of the Ingulets River are significantly overfilled with chlorides, sulfates, nitrates, nitrites, and other pollutants [17].

Based on the description of various methods of water desalination, the following conclusions can be drawn. Of all the above methods of water desalination, the only potentially technically and economically feasible method in this case is reverse osmosis combined with evaporation and crystallization.

These methods are the most commonly used technologies for conditions similar to mine water conditions in the Kryvyi Rih iron ore basin.

The use of the technology has several advantages:

– water does not undergo phase transitions (evaporation or freezing), which ensures low energy costs when using this method, in comparison with other known demineralization technologies;

– high selectivity of polyamide membranes (96-99.8%);

– relatively low operating costs;

– simplicity of the technological process;

– technically simple control over the quality of purified water (for example, electrical conductivity);

– reverse osmosis provides complete bactericidal treatment of water due to the combined processes of demineralization and disinfection, as a result of the small diameter of the membrane pores, which do not let in not only salt ions, but also bacteria, spores and viruses. However, when water is discharged into the water supply system, it must undergo disinfection.

The technological process of purification of mineralized mine waters of mining enterprises of the Kryvyi Rih iron ore basin includes the following main stages:

– receiving and averaging of incoming mine water;

– reagent lime-soda softening and clarification of mine water, which is supplied for treatment, with separation of the resulting suspension by settling and additional filtration on granular filters;

– membrane desalination of mine waters with preliminary pH adjustment;

– treatment of reverse osmosis concentrate by evaporation on an evaporator unit;

– concentration of saturated brine after the evaporation unit in a vacuum crystallizer;

– centrifugation of a suspension of crystalline salts (sodium chloride);

– final drying of crystalline salts (sodium chloride) to a moisture content of 15-20%.

The proposed technology for the complex processing of highly mineralized mine waters of the mining enterprises of the Kryvyi Rih iron ore basin is shown in Fig. 1.

The proposed technology for the complex processing of highly mineralized mine waters, which are pumped to the surface by the mining enterprises of the Kryvyi Rih iron ore basin, will work 24 hours a day, 365 days a year.

The supply of highly mineralized mine water for processing is 16 million m^3/year. The average value of the total mineralization is taken to be 40 g/dm^3 [4].

In the process of mine water preliminary treatment in contact clarifiers, suspended and colloidal substances, calcium and magnesium compounds are removed from the effluents, which will be concentrated in the sludge fraction. The specified sludge after compaction and filtering on a filter press can be used as a raw material for the manufacture of cement and other construction mixtures.

During the reverse osmosis process, approximately three-quarters of the water used for desalination are con-

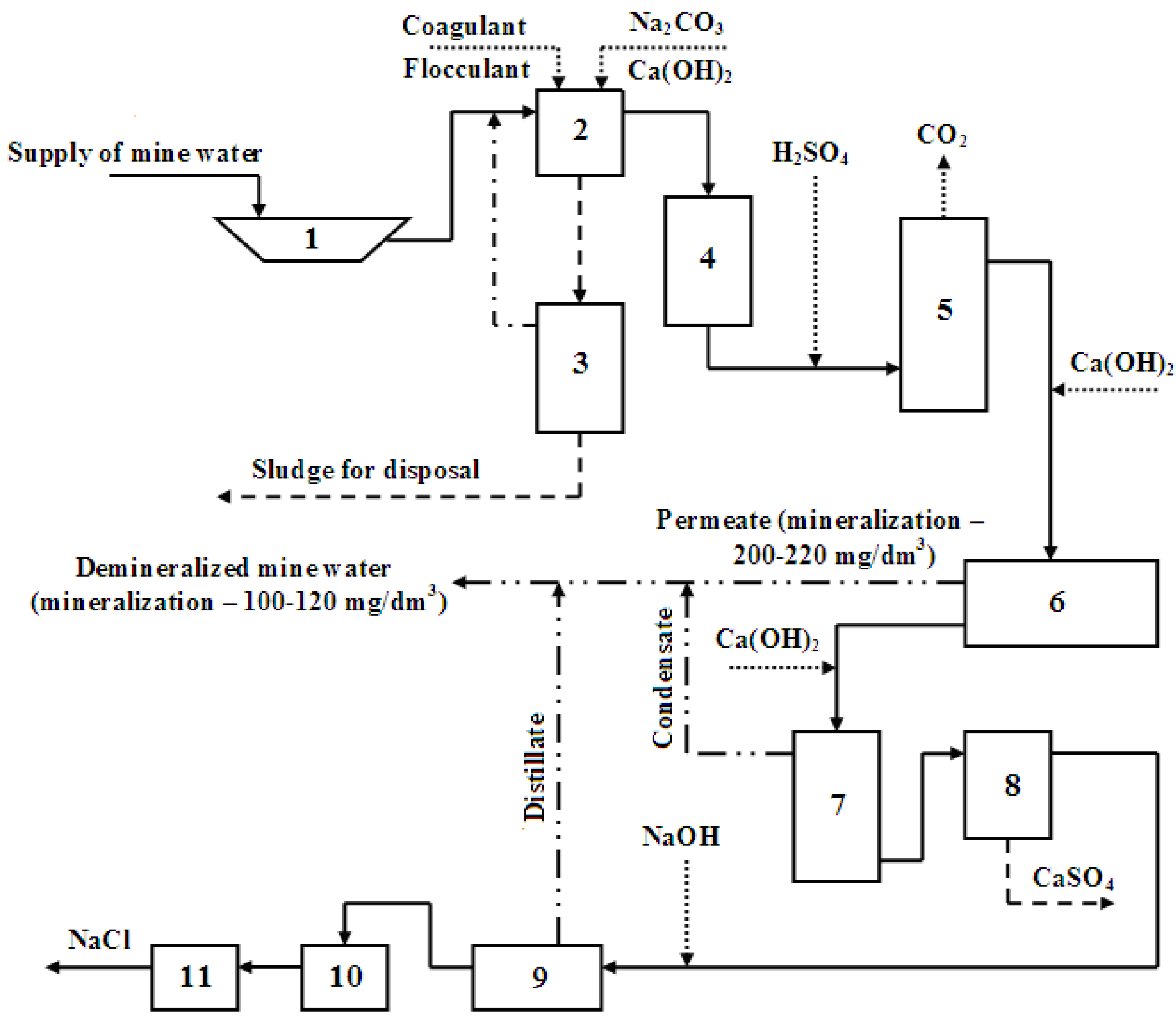

Fig. 1. Resource-saving technology of complex processing of highly mineralized mine waters of mining enterprises of Kryvyi Rih iron ore basin

1 – mine water storage pond; 2 – contact clarifier for wastewater; 3 – coagulation sludge press filter; 4 – two-layer filter with granular loading; 5 – decarbonizer; 6 – reverse osmosis plant; 7 – evaporation plant; 8 – clarifier for settling calcium sulfate crystals; 9 – crystallizer; 10 – salt sludge dewatering centrifuge; 11 – dryer

verted to demineralized water. We accept that this value will be approximately 70%. Thus, at the outlet of the reverse osmosis unit will be formed approximately 11.2 million m^3/year of demineralized water and 4.8 million m^3/year of highly concentrated brine, respectively.

The resulting highly mineralized brine (with a salt content of about 80 g/dm^3) enters the last stage of the desalination process – evaporation/crystallization. During this process, approximately 93.5% of the consumption of highly concentrated salt solution entering the crystallizer is converted to demineralized water. Thus, at the outlet of the vacuum crystallizer will be formed approximately 4.49 million m^3/year of demineralized water and 0.31 million m^3/year of solid salt product, respectively. At the same time, the average allowable density of the salt (solid product) is 2.16 kg/dm^3. Therefore, the approximate amount of solid product (mineral salts) formed after the complex processing of highly mineralized mine waters of the mining enterprises of the Kryvyi Rih iron ore basin using the proposed technology will be about 669,600 tons.

The product obtained in the course of complex processing is a mixture of mineral salts, mainly sodium chloride, which can later be used as a water softening agent or in public utilities as a technical salt.

In addition, calcium sulfate (the so-called alabaster, gypsum), which is released from a concentrated salt solution after evaporation in a clarifier, can be used later in construction for the manufacture of dry plaster, slabs and panels for partitions, etc. It can also be used in medicine for the manufacture of plaster bandages, which provides the fixation of individual parts of the body, and in art, mainly in sculpture and architecture.

Thus, after the complex processing of highly mineralized mine waters using the proposed technology, approximately 15.69 million m^3 of demineralized water and about 0.31 million m^3 of solid salt product will be obtained, which, in terms of mass, will be 670 thousand tons.

Consequently, the proposed technology for the complex processing of highly mineralized mine waters can be considered practically waste-free, since all impurities are removed from the water in the form of valuable raw materials.

Conclusions. The paper solves an urgent practical problem, which consists in the development of a resource-saving technology for the complex processing of highly mineralized mine waters of the mining enterprises of the Kryvyi Rih iron ore basin.

After complex processing of highly mineralized mine waters using the proposed technology, approximately 15.7 million m^3 of demineralized water with a salt content of 0.1-0.5% of their initial concentration and about 0.31 million m^3 of solid salt product will be obtained, which, in terms of mass, will be 670 thousand tons.

Perspectives for the further use of research results. The introduction of the proposed technology makes it possible to obtain demineralized water, the hydrochemical parameters of which correspond to the quality standards of surface water bodies, and marketable mineral products that can be used as valuable raw materials for the needs of the national economy.

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