ЕКОЛОГІЯ

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Karina BELOKON

Candidate of Technical Science, Associate Professor, Deputy Director for Research of the Engineering Educational and Scientific Institute by name of Yu.M. Potebnya, Part-Time Associate Professor at the Department of Metallurgical Technologies, Ecology and Technogenic Safety, Zaporizhzhia National University, 66 Universytetska str., Zaporizhzhia, Ukraine, 69011

ORCID: 0000-0003-2000-4052 **Scopus Author ID:** 56196099400

Genadij KOZHEMYAKIN

Candidate of Technical Science, Associate Professor, Associate Professor at the Department of Metallurgical Technologies, Ecology and Technogenic Safety, Zaporizhzhia National University, 66 Universytetska str., Zaporizhzhia, Ukraine, 69011

ORCID: 0000-0002-2960-1331 Scopus Author ID: 57191165525

Vladyslav BENDIUH

Candidate of Technical Science, Associate Professor, Associate Professor at the Department of Artificial Intelligence, Educational and Research Institute for Applied System Analysis, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», 37 Beresteiskyi ave., Kyiv, Ukraine, 03056

ORCID: 0000-0003-3295-4637 **Scopus Author ID:** 57433852300

Bohdana KOMARYSTA

Candidate of Technical Science, Associate Professor, Associate Professor at the Department of Artificial Intelligence, Educational and Research Institute for Applied System Analysis, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», 37 Beresteiskyi ave., Kyiv, Ukraine, 03056

ORCID: 0000-0001-9542-6597 **Scopus Author ID:** 26654832900

Mykyta ZHAVORONKOV

Postgraduate Student at the Department of Metallurgical Technologies, Ecology and Technogenic Safety, Engineering Educational and Scientific Institute by name of Yu. M. Potebnya, Zaporizhzhia National University, 66 Universytetska str., Zaporizhzhia, Ukraine, 69011

ORCID: 0009-0009-5396-8406

Ihor KARIYAKA

Graduate student of the Department of Metallurgical Technologies, Ecology, and Technogenic Safety, Institute by name of Yu.M. Potebnya, Zaporizhzhia National University, 66 Universytetska str., Zaporizhzhia, Ukraine, 69011

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STUDY OF THE THERMAL TREATMENT METHOD FOR HIGHLY MINERALIZED WASTEWATER FROM INDUSTRIAL PRODUCTION

Highly mineralized wastewater from industrial enterprises is one of the main pollutants of the natural environment. This type of liquid waste is contaminated with mineral substances such as salts of calcium, sodium, magnesium, etc. Despite the widespread implementation of recirculating water supply and new low-waste technologies, the volume of contaminated wastewater remains significant. Therefore, the purification of liquid waste from mineral contaminants is a major problem.

A method for thermal neutralisation of highly mineralised liquid industrial waste using intermediate solid heat transfer has been proposed, offering promising prospects for application in metallurgy, chemistry, coal mining, energy and other industrial sectors. Laboratory equipment was developed, with an electric heater and an evaporation column containing an inert heat transfer medium in the form of metal balls. This work investigated the hydrodynamic regime of the evaporation apparatus during the disposal of highly mineralized wastewater on an intermediate solid heat carrier. Experiments were conducted on a granular packing with ball diameters of 10 and 15 mm. During the evaporation process, water was fed cyclically at a speed of 2, 2.5, and 3 m/s. As a result, it was found that the hydraulic resistance of the evaporation apparatus depends on the speed of the hot heat carrier and the type of packing (dry or wet).

The conducted laboratory studies showed that the cyclical evaporation of highly mineralized wastewater using an intermediate solid heat carrier (metal balls) allows for reduced energy consumption and the effective removal of mineral contaminants from the water. However, the formation of a salt film on the packing elements reduces the porosity of the layer and increases hydraulic resistance. To ensure the efficient operation of the evaporation apparatus, it is necessary to maintain an optimal level of porosity.

Key words: liquid waste, wastewater, thermal treatment, brines, evaporation, evaporators, intermediate heat carrier, hydraulic resistance.

Каріна БЄЛОКОНЬ

кандидат технічних наук, доцент, заступник директора з наукової роботи Інженерного навчальнонаукового інституту імені Ю.М. Потебні, доцент кафедри металургійних технологій, екології та техногенної безпеки за сумісництвом, Запорізький національний університет, вул. Університетська, 66, м. Запоріжжя, Україна, 69011

ORCID: 0000-0003-2000-4052 **Scopus Author ID:** 56196099400

Геннадій КОЖЕМЯКІН

кандидат технічних наук, доцент, доцент кафедри металургійних технологій, екології та техногенної безпеки, Запорізький національний університет, вул. Університетська, 66, м. Запоріжжя, Україна, 69011

ORCID: 0000-0002-2960-1331 **Scopus Author ID:** 57191165525

Владислав БЕНДЮГ

кандидат технічних наук, доцент, доцент кафедри штучного інтелекту Навчально-наукового інституту прикладного системного аналізу, Національний технічний університет України «Київський політехнічний інститут імені Ігоря Сікорського», пр. Берестейський, 37, м. Київ, 03056

ORCID: 0000-0003-3295-4637 **Scopus Author ID:** 57433852300

Богдана КОМАРИСТА

кандидат технічних наук, доцент, доцент кафедри штучного інтелекту Навчально-наукового інституту прикладного системного аналізу, Національний технічний університет України «Київський політехнічний інститут імені Ігоря Сікорського», пр. Берестейський, 37, м. Київ, 03056

ORCID: 0000-0001-9542-6597 **Scopus Author ID:** 26654832900

Микита ЖАВОРОНКОВ

аспірант кафедри металургійних технологій, екології та техногенної безпеки Інженерного навчальнонаукового інституту імені Ю.М. Потебні, Запорізький національний університет, вул. Університетська, 66, м. Запоріжжя, Україна, 69011

ORCID: 0009-0009-5396-8406

Ігор КАРЯКА

здобувач вищої освіти кафедри металургійних технологій, екології та техногенної безпеки Інженерного навчально-наукового інституту імені Ю.М. Потебні, Запорізький національний університет, вул. Університетська, 66, м. Запоріжжя, Україна, 69011

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Одними з основних забруднювачів навколишнього природного середовища є високомінералізовані стічні води промислових підприємств. Цей вид рідких відходів забруднений такими мінеральними речовинами, як солі кальцію, натрію, магнію тощо. Попри широке впровадження оборотного водопостачання та нових маловідходних mехнологій, обсяг забруднених стічних вод залишається значним. Тому важливою проблемою ϵ очищення рідких відходів від мінеральних забруднень. Запропоновано спосіб термічного знешкодження високомінералізованих рідких відходів промислових виробництв на проміжному твердому теплонасії, який є перспективним для застосування в металургійній, хімічній, вугільній, енергетичній та інших промислових галузях. Було створено лабораторну установку, що складається з електропідігрівача і випарної колони, в якій знаходиться інертний теплоносій у вигляді металевих куль. У роботі було досліджено гідродинамічний режим випарного апарату при знешкодженні високомінералізованих стічних вод на проміжному твердому теплоносії. Досліди були проведені на зернистій насадці з різними діаметрами куль 10 та 15 мм. У процесі випарювання вода подавалася циклічно зі швидкістю 2, 2,5 та 3 м/с. Внаслідок чого було виявлено, що гідравлічний опір випарного апарату залежить від швидкості гарячого теплоносія та типу насадки (суха або мокра). Проведені лабораторні дослідження показали, що циклічне випарювання високомінералізованих стічних вод з використанням проміжного твердого теплоносія (металевих куль) дозволяє знижувати енергетичні витрати та ефективно вилучати мінеральні забруднення з води. Однак, утворення плівки солей на елементах завантаження знижує порізність шару і підвищує гідравлічний опір. Для забезпечення ефективної роботи випарного апарату необхідно підтримувати оптимальний рівень порізності.

Ключові слова: рідкі відходи, стічні води, термічне знешкодження, розсоли, випарювання, випарні установки, проміжний теплоносій, гідравличний опір.

Urgency of the problem. One of the main challenges in modern industry is the development of measures to protect the environment from pollutants that enter water bodies and soils with industrial wastewater. In this regard, an important task is the treatment of industrial wastewater and the replenishment of fresh water resources through its purification. Despite the widespread implementation of water recycling systems and new low-waste technologies, the amount of contaminated industrial wastewater remains significant (Khanafer D. et al., 2024).

Common components of industrial wastewater are various mineral substances, such as calcium, sodium, and magnesium salts. They are formed either as a result of neutralization reactions involving acids and alkalis, which are frequently used in metallurgical production, or during the purification of various gases (Hafiz Zahid Shafia et al., 2018). In addition, mineral contaminants enter wastewater through the contact of liquids with various products containing salts in a solid state or in solution. Mineralized solutions are also formed in systems for the treatment of industrial wastewater containing acids, alkalis, and organic compounds (Kumar Avinash et al., 2023).

The currently developed plants for purifying water from these substances produce solutions and sludges that, in a number of cases, cannot be discharged into natural sources and must be neutralized. The growth in the production of various industrial goods leads to an increase in the amount of mineralized wastewater discharged. This increases the concentration of salts in water bodies and soil, causing irreparable damage to the environment. Therefore, the problem of purifying

highly mineralized wastewater must be solved only by considering the utilization of the resulting brines.

It should be noted that the underground disposal of brines is associated with many negative consequences, some of which are already being observed, while others may manifest in the distant future. For example, due to the migration of groundwater and tectonic changes in the earth's crust, brines may appear in water intake wells located far from their injection site. Therefore, the best option when treating highly mineralized liquid waste is to obtain solid salts rather than highly concentrated brines, which is convenient for both transportation and disposal.

In ferrous metallurgy enterprises, the concentration of salts in water increases due to the use of soluble substances in metallurgical technology and water treatment, leaching in water processes, and evaporation in water supply systems. The main sources of highly mineralized liquid waste are water treatment plants (WTP); steam generators (blowdown water); pickling departments (rinse water after pickling and degreasing); mining and ore enterprises (quarry and mine water); and local water supply systems (blowdown water) (Ostapenko, N. et al., 2019).

The listed sources can be conditionally classified as sources with controlled discharge; besides them, there are uncontrolled ways of removing

salts from water supply systems – wind drift, filtration from hydraulic structures, removal with moist slag and sludge, and others (Iliev I. K. et al., 2023). Approximately 80% of the total amount of salts discharged in the industry as a whole, and about 60% at enterprises with a full metallurgical cycle, is removed through controlled discharge. A general characteristic of mineralized wastewater from ferrous metallurgy enterprises is given in Table 1.

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Table 1
General characteristics of mineralized liquid waste from ferrous metallurgy enterprises

Type of Wastewater, Source of Origin	Annual Discharge, million m ³	Share in Total Salt Discharge, %	Composition of Main Salt Components	
Regeneration and rinse waters from sodium-cation filters	30	13.30 – 15.30	NaCl, CaCl ₂ , MgCl ₃	
The same, hydrogen-cation filters	2	0.56 - 0.58	${ m CaSO_4, MgSO_4,} \ { m Na_2SO_4}$	
The same, ion-exchange desalinating units	3	1.10 – 1.15	${ m CaSO_4, MgSO_4,} \ { m Na_2SO_4, NaCl,} \ { m Na_2SiO_3}$	
Blowdown waters of steam generators	40	5.60 – 7.70	Na ₂ SO ₄ , NaCl, Na ₂ CO ₃ , NaOH, Na ₂ SiO ₃ , Na ₃ PO ₄	
Neutralized rinse waters after metal pickling	25	5.20 – 5.40	CaSO ₄ , Na ₂ SO ₄ , NaCl, CaCl ₂ , Ca(NO ₃) ₂ , NaNO ₃	
Rinse waters after metal degreasing	5	0.56 - 0.77	Na ₂ CO ₃ , NaOH, Na ₃ PO ₄ , Na ₂ SiO ₃	
Blowdown waters of local water supply systems	50	18.50 – 19.20	Na ₂ SO ₄ , NaCl, CaSO ₄ , Ca(HCO ₃) ₂ , Mg(HCO ₃) ₂	
Quarry and mine waters of mining enterprises	150	51.80 - 53.70	NaCl, Na ₂ SO ₄ , CaSO ₄ , MgSO ₄ , K ₂ SO ₄ , Ca(HCO ₃) ₂ , Mg(HCO ₃) ₂	

the best option when treating highly mineralized wastewater is to obtain not highly concentrated brines, but solid salts, which is convenient for both transportation and disposal (Reinvald B. S. et al., 2023, Yalova A. M. & Bondar N. V., 2024).

Analysis of recent research and publications. Many scientists are engaged in research on water purification. Their work is aimed at increasing the efficiency of water treatment in various sectors of the economy.

To protect the environment from pollution by insufficiently treated wastewater, it has been proposed to improve the technology of coagulation water treatment, in particular, the use of the sodalime method in natural water purification systems (Trofimenko M. O. et al., 2011). However, according to the authors of the study, the implementation of this technology is not possible without prior refinement in the wastewater treatment technology, which has a significant impact on the process efficiency.

The main problem is the presence of impurities in the wastewater that are not incorporated into the crystal structure of the precipitate during crystallization. These impurities require an additional amount of reagents compared to classic doses, which, in turn, increases the cost of the purification process. Considering this, the authors propose a new approach for a more accurate calculation of the required amount of reagents, particularly soda, when using the soda-lime method for treating wastewater with a high salt content.

The proposed formula takes into account the amount of magnesium contained in the wastewater and allows for an adjustment to calculate the additional dose of soda. This is particularly relevant when the magnesium content exceeds 10% of the calcium content in the water. Calculations based on this formula can significantly increase the accuracy of reagent dosing and, consequently, improve the efficiency of the water softening process.

An important aspect of the work is identifying the impact of additional magnesium impurities on the purification process, which helps to optimize technological parameters and reduce reagent costs. The authors emphasize that to achieve effective water purification, it is necessary to consider not only traditional parameters but also the specific properties of the wastewater, such as magnesium content.

The works of I. M. Trus et al. (Trus I. M. & Homelia D. M., 2021, Trus I. M. et al. 2020) are

dedicated to the development of methods for the stabilization treatment of low- and high-mineralized waters in baromembrane desalination processes to increase purification efficiency and extend the service life of membranes. The work considers the use of various membranes and reagents to improve the results of baromembrane water desalination.

Specifically, for the purification of low-mineralized waters and waters with a NaCl concentration of up to 10%, the authors recommend using the weakly acidic cation exchanger Dowex MAC-3. This cation exchanger effectively removes hardness ions, which improves water quality at the pretreatment stage before membrane processes. However, for the desalination of highly mineralized waters with higher levels of mineralization, the authors suggest using the reverse osmosis membrane Filmtec TW30-1812-50, which provides effective salt removal from water. For the purification of low-mineralized waters, the nanofiltration membrane OPMN-P is more suitable.

One of the important aspects of the work is the treatment of concentrates formed during baromembrane purification processes. The authors recommend using reagent methods to reduce the mineralization of solutions to levels permissible for discharge into sewers or surface water bodies. This helps to reduce the environmental impact and facilitate the disposal of waste from baromembrane processes.

To achieve maximum purification efficiency, work (Salli V. S. et al., 2020) proposes the use of reverse osmosis, with a comprehensive pretreatment process applied before the main desalination process. This complex includes the following stages: screening, coagulation, flocculation, softening, and sedimentation (settling) of water. This prepares the water for treatment by reverse osmosis membranes, which are vulnerable to high turbidity, the presence of chlorides, heavy metals, organic compounds, and hard water.

The application of such an approach significantly increases the efficiency of mine water purification, which allows for the evaluation of mine water not only as waste but also as a potential resource for further use. As a result, the proposed technology is of great importance for improving the environmental efficiency and economic benefits of mine water treatment, especially in the context of mine closures and the possibility of their preservation.

All these studies in the field of purification are important for improving the ecological state of water resources, reducing the impact on the environment, and increasing the efficiency of industrial processes (Bosiuk A. & Shestopalov O., 2023). The implementation of such technologies will help solve the problem of utilizing highly mineralized liquid waste and ensure the sustainable development of industrial enterprises, taking into account modern environmental standards (Strutynska, A. V. et al., 2009, Budenkova N. M. & Korchyk N. M., 2023).

However, the wide variety of salt compositions in wastewater and the differences in the capacity and intended purpose of treatment plants do not allow for the selection of a single universal purification method that could be applied with maximum economic efficiency in virtually any conditions.

Currently, a large number of different types of plants for the treatment of highly mineralized liquid waste have been created, differing from each other in the organization of the boiling process, the pressure at which the distillation process occurs, heat regeneration, the concentration factor of the purified water, the connection to the power plant cycle, the structural design, and a number of other features.

One attempt to increase the efficiency of treating concentrated solutions is associated with the creation of multi-stage plants in which the solution is heated or evaporated upon contact with hydrophobic heat carriers. The problem of scaling does not arise in such surface-free evaporation plants, as heat transfer in them occurs through direct contact between the heated heat carrier and the water being purified.

During preliminary experiments, good results were obtained when using granulated blast-furnace slag from the «Zaporizhstal» plant as a packing material for the maximum deposition of salts. The wastewater used was from the Zaporizhzhia Titanium-Magnesium Plant with a salt content of 12–15 g/L. The maximum possible amount of salts deposited in the bed was 20–23% of the packing weight. However, this packing has the following disadvantages: the difficulty of separating the precipitated salts from the slag; during the irrigation of the slag with the solution, it breaks down, and fine particles are carried away with the solution, leading to contamination of the effluent.

These disadvantages are substantially eliminated by using metal balls as the intermediate heat

carrier packing. They are convenient for processing in a ball mill and have good thermal conductivity. The mass of salt deposits is 8–10% of the packing mass.

The process of evaporating highly mineralized solutions can be divided into three stages: heating the balls with hot gas; irrigating the balls with the solution, which leads to their cooling and partial evaporation of the solutions; and evaporating the solution from the surface of the intermediate heat carrier. The limiting stages in terms of time and heat transfer conditions are the first and third.

Based on the research, a principal technological scheme for a plant for treating highly mineralized wastewater is proposed (Fig. 1). The intermediate heat carrier, consisting of metal balls with a diameter of 10–20 mm, is placed in a heating chamber on a grid.

Hot gas is supplied to the chamber, heating the bed of the granular intermediate heat carrier. The solution is supplied through nozzles in portions, as the packing dries. The application of the solution to the bed leads to its partial evaporation and the cooling of the balls. A film of crystals, covered by a layer of moisture, forms on the surface of the grains. As it dries, the layer of crystals grows. The amount of salts deposited on the solid intermediate heat carrier in one cycle is small, so the solution is applied several times. After this, the ball packing with the film of salt crystals is removed from the heating chamber and sent for mechanical processing in a ball mill. The extracted metal balls are returned to the desalination cycle after regeneration.

The heat transfer coefficient for this plant design is in the range of 80–120 W/m²·K. In plants with a fluidized bed, this coefficient is in the range of 65–100 W/m²·K. The energy consumption in this process is about 1600–1800 kJ/kg of evaporated moisture, and according to expert estimates, it could be around 550 kJ/kg of evaporated water in the future.

Thus, the above-considered plant for the treatment of highly mineralized wastewater is the most effective and promising, as it eliminates the disadvantages of plants with a liquid hydrophobic heat carrier, namely: metal balls, unlike a viscous heat carrier, are not difficult to separate from salt crystals; high intensity of heat exchange due to the high thermal conductivity of the heat carrier; the need to separate the heat carrier from the solution is eliminated.

The advantages of the plant are: high evaporation intensity with periodic solution feed; low energy consumption, as the largest layer of product builds up with periodic circulation; the metal balls do not break down and contaminate the effluent when irrigated with the solution; in the ball mill, the balls are not destroyed during cleaning from scale due to their strength; this treatment method allows the use of secondary low-potential energy resources.

The developed method for treating highly mineralized liquid waste is promising for application in various industries. The use of thermal treatment with an intermediate solid heat carrier can significantly increase the efficiency of the purification process, reduce energy costs, and minimize the environmental impact.

Results and discussion. To study the hydrodynamic processes of evaporating highly mineralized wastewater on an inert intermediate heat carrier, a laboratory setup was created, the scheme of which is shown in Fig. 2.

The laboratory setup consists of an electric heater 1 and an evaporation column 4, which contains an inert heat carrier 6 in the form of metal balls with a diameter of 10–15 mm. The supplied air is heated in the heater 1 and fed through a pipe 2 and a grid 5 into the chamber 4. The solution from the circulation tank 7, under pressure created by the air pump 10, is fed into the column 4, where part of it evaporates, and part flows down through the distribution chamber 3 and the hydraulic seal 8 into a measuring vessel 9. The water remaining

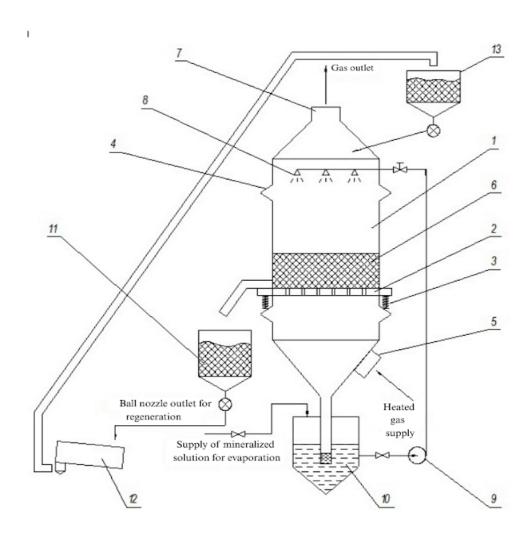


Fig. 1. Principal technological scheme for evaporating highly mineralized wastewater using an intermediate solid heat carrier 1 – heating chamber; 2 – support grate; 3 – springs; 4 – compensator; 5 – gas inlet pipe; 6 – ball nozzle; 7 – gas outlet pipe; 8 – irrigation system; 9 – pump; 10 – circulation tank; 11 – bunker for receiving balls for regeneration; 12 – ball mill; 13 – balls after regeneration

on the heat carrier is evaporated by the incoming heated air.

Air, preheated by an electric heater to a temperature of at least 200°C, is supplied to the heating chamber. The heated air, passing through the layer of balls, gives off heat and is discharged through a pipe. The heated air is supplied by a fan through the pipe until the air temperature at the outlet of the pipe is not less than 110°C and the average temperature of the packing is 140°C. The higher the temperature of the balls, the more intense the evaporation. With continuous heating of the intermediate heat carrier, after reaching the required temperature of the balls, we perform cyclic irrigation of the packing with the solution until the concentration of the solution at the outlet of the chamber is equal to or slightly exceeds the concentration of the solution at the inlet to the heating chamber. In this process, part of the water evaporates, part wets the packing, and the remaining water returns to the circulation tank. Under the action of the hot gaseous heat carrier, film evaporation of the mineralized solution first occurs, forming a salt scale on the surface of the metal balls, and then the balls of the solid heat carrier are heated. Then the process is repeated.

The study investigated the hydrodynamic regime of the evaporation apparatus during the treatment of highly mineralized wastewater on an intermediate solid heat carrier. The experiments were conducted on a granular packing with different ball diameters of 10 and 15 mm. During the evaporation process, water was supplied cyclically at speeds of 2, 2.5, and 3 m/s. As a result, it was found that the hydraulic resistance of the evaporation apparatus depends on the speed of the hot heat carrier and the type of packing (dry or wet).

All controlled parameters during the experiment are recorded in Table 2. The dependence of the increase in the hydraulic resistance of the heat carrier bed on the gas flow velocity is presented in Fig. 3.

During the laboratory study, a dependency was observed—as the speed of the hot heat carrier increased, the hydraulic resistance of the evaporation apparatus also increased. Moreover, on balls with a diameter of 10 mm, the increase in resistance was greater than on the packing with a ball diameter of 15 mm. The porosity of the bed between balls with a diameter of 10 mm decreases faster than with a diameter of 15 mm as the speed of the hot heat carrier increases.

A dependence of the hydraulic resistance on the type of packing was also observed. The hydraulic resistance of the evaporation apparatus increases faster on wet packing than on dry packing. This is because when the balls are irrigated with the solution, the liquid fills the voids between the balls, which reduces the porosity of the bed and increases the hydraulic resistance.

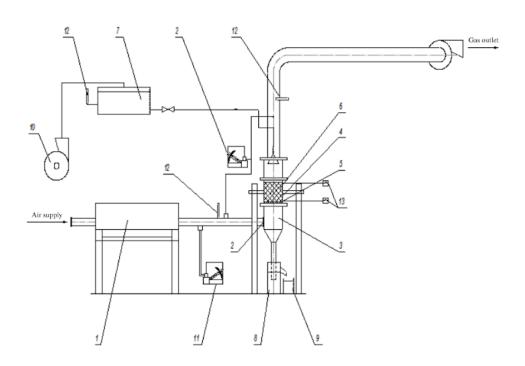


Fig. 2. Laboratory setup for evaporation of highly mineralized wastewater

Table 2

Results of experimental studies

№ Ball diamet	D 11 11	Gas velocity, W _g , m/s	Nozzle Type	Hydraulic Resistance	
	Ball diameter, d, mm			Δp , Pa	Δp_a , Pa
1	10	2	dry	17	17
2			wet	20	
3				22	
4				26	25
5				28	
6				31	
7		2,5	dry	48	48
8			wet	54	
9				67	
10				81	81
11				98	
12				104	
13		3	dry	109	109
14			wet	127	176
15				153	
16				175	
17				203	
18				224	
19		2	dry	15	15
20			wet	18	23
21				21	
22				23	
23				25	
24				28	
25		2,5	dry	36	36
26			wet	42	62
27				51	
28	15			62	
29				73	
30				82	
31		3	dry	96	96
32			,	105	_
33			wet	127	
34				149	147
35				163	1
36				192	

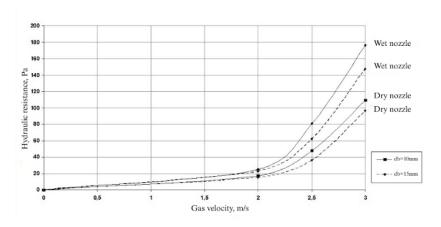


Fig. 3. Dependence of the growth of hydraulic resistance of the coolant layer on the gas flow rate

Overall, according to the research results, the cyclic evaporation of highly mineralized solutions on an intermediate solid heat carrier leads to the formation and growth of a salt film on the packing elements. Thus, the porosity of the bed decreases to a critical value, and the hydraulic resistance of the intermediate solid heat carrier increases. For the further effective operation of the evaporation apparatus, it is necessary that the porosity of the granular bed during the evaporation process be as large as possible above its critical value. Therefore, the intermediate solid heat carrier must be regenerated – removed from the apparatus and sent for mechanical processing to remove the salt layer. It is then reused for evaporation.

Conclusions and directions for future research. The creation of effective systems for treating industrial wastewater is important for many industries: metallurgical, chemical, coal, energy, and others. The wide variety of salt compositions in wastewater and the differences in the capacity and intended purpose of treatment plants do not allow for the selection of a single universal purification method.

The use of most traditional methods for treating highly mineralized liquid waste is usually associated with the need to solve a number of problems, the main ones being the disposal of highly concentrated brines, the high cost of desalination, and high energy consumption. However, the most promising method is thermal treatment using an intermediate

heat carrier and utilizing secondary low-potential energy resources. Thanks to this, the problem of scale formation is eliminated, as the technological process ensures the targeted deposition of salts on the packing bed.

As an intermediate heat carrier, it is most acceptable to use metal balls, as they are convenient for processing in a ball mill, have good thermal conductivity and strength. The main advantage of this method is the ability to extract mineral contaminants contained in wastewater in solid form, as well as the use of secondary low-potential energy resources as a heat carrier.

The main characteristics of the heat carrier that affect the hydrodynamic regime of the evaporation apparatus were considered. To study this regime of evaporating highly mineralized wastewater on an intermediate solid heat carrier, a laboratory setup was manufactured, and a methodology for conducting the evaporation process was determined. According to the research results, the cyclic evaporation of highly mineralized solutions on an intermediate solid heat carrier leads to the formation and growth of a salt film on the packing elements. Thus, the porosity of the bed decreases to a critical value, and the hydraulic resistance of the intermediate solid heat carrier increases. For the further effective operation of the evaporation apparatus, it is necessary that the porosity of the granular bed during the evaporation process be as far as possible above its critical value.

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