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Research on purification of tailings solutions from metal impurities at lead dust processing enterprises

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Abstract

Purpose. The research aims to develop a technology for tailings solution purification using membrane nanofiltration to reduce waste volume and enterprise costs by reusing the purified water.

Methods. The research uses polyamide nanofiltration membranes on a semi-industrial plant. The nanofiltration process is conducted at a pressure of 3.5 MPa with 30% permeate yield. The chemical composition of the solutions is analyzed using atomic-absorption and chemical methods.

Findings. Removal of 69% arsenic, 68.5% zinc and 95.7% iron has been achieved under optimal conditions. The purified solution with a residual sulphuric acid concentration of ~3.5 g/l can be used again for leaching lead dust. The concentrated metal solution allows for additional zinc extraction. The use of technology reduces waste volumes by more than 30% and reduces the enterprise's recycling costs.

Originality. The research proposes a new environmentally friendly nanofiltration technology for tailings solution purification that can effectively remove heavy metals and extract valuable components. This approach uniquely integrates membrane nanofiltration at an optimized pressure of 3.5 MPa, achieving high removal rates of heavy metal ions such as As^{3+}, AsO_4^{3-}, Zn^{2+}, Fe^{2+}, and Fe^{3+}, while reducing waste by 30% and enabling the reuse of sulfuric acid and water in the leaching process, leading to significant cost and resource savings.

Practical implications. Implementation of the proposed technology at lead dust processing enterprises reduces the costs of wastewater treatment, reduces the waste volume and allows for the reuse of water and acids in the production process.

Keywords: *membrane nanofiltration, heavy metals, wastewater treatment, lead dust, resource saving, extraction of valuable components*

1. Introduction

Kazakhstan's mining industry plays a central role in the country's economic development, contributing significantly to its Gross Domestic Product (GDP) and providing the basis for industrial growth and exports [1], [2]. Kazakhstan is one of the world's leading countries in mining minerals such as copper, lead, zinc, uranium and rare-earth metals, making it an important player in the global market [3], [4]. The country's fields have unique reserves of resources that are actively used in the metallurgical, chemical and machine-building industries [5]. With a strong mineral resource base and growing demand for metals, especially given the development of technologies and increasing need for raw materials for the production of electronics, energy and transport, Kazakhstan is well positioned for continued dynamic growth in the mining sector [6].

At the same time, production growth is accompanied by serious environmental challenges, especially in the context of sustainable waste management and minimizing environmental impact [7]. Ore and metal processing processes inevitably generate significant volumes of industrial wastewater containing heavy metals, acids and other toxic substances [8]-[10]. These wastes pose a risk to both ecosystems and human health. In particular, lead and arsenious compounds, which are often found in processed products, require special treatment and disposal methods to prevent their release into water and soil resources. In the context of the global trend towards more environmentally friendly production, environmental protection issues are becoming an integral part of the sustainable development of the mining industry, requiring the introduction of innovative technologies to effectively recycle waste and minimize environmental damage [11]-[13].

Modern approaches to waste management in the mining industry are oriented towards the use of state-of-the-art technologies for wastewater treatment and reuse, which also allows for the extraction of valuable components from waste [14], [15]. Membrane technologies, in particular nano-

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filtration, are becoming increasingly in demand due to their ability not only to purify industrial water from heavy metals, but also to reduce processing costs by returning purified solutions to the production process, which is especially important for enterprises working with highly toxic waste such as lead dust [16], [17].

At present, the generation of industrial wastewater from metallurgical enterprises is one of the urgent problems of liquid waste utilization in various areas of national economy, as emissions contain pollutants that pose a threat to human health, ecology and biodiversity on Earth [18]. Mining, pharmaceutical, textile, agro-industrial, plastics and other industries produce a large amount of wastewater containing hazardous pollutants that have a negative impact on the environment [19]. The composition and concentration of harmful impurities in industrial wastewater depends on the type of processed raw materials, availability of treatment facilities and filtering equipment [20], [21]. Wastewater composition is also affected by the nature of the technological processing process, the composition of the initial mineral raw materials, intermediate products, output products, water composition, as well as the characteristics of equipment and other factors [22]-[24].

The lead dust processing enterprise at the Balkhash Copper Smelting Complex extracts metallic lead and copper as commercial products from arsenious lead dust. As a result of hydrometallurgical processing, large volumes of tailings solutions are generated. This requires disposal or burial as solid waste, or additional processing of recycled liquors for neutralization and reuse. However, the utilization of tailings solutions requires large amount of lime milk and associated costs to construct and maintain a tailings dam. In this case, the reuse of industrial wastewater depending on the degree of purification determines the quality and cost of the resulting commercial products [24]-[27].

Conventional technologies for wastewater treatment from hazardous pollutants such as heavy metals, organic pollutants, dyes, micro plastics and nanoplastics involve physical, chemical, biological methods to reduce the concentration of pollutants [28]. Processes may include gravitational settling of solids and suspended particles using coagulants, adsorption of polluting elements depending on their properties with ion-exchange sorbents [29], [30]. However, this requires complex technological processes involving large amounts of chemical reagents, electricity and labor to remove pollutants from the water.

In recent years, significant attention has been paid to the use of nanomembranes for the purification of process solutions and wastewater from enterprises [31]-[33]. The nanofiltration process is performed at medium to high pressure. In essence, nanofiltration is a process similar to reverse osmosis process, where the membrane has a slightly more open structure, allowing monovalent ions to pass through it.

The potential of nanomembranes in various solution treatment applications, such as water purification and desalination was studied in [34]-[39]. These nanomembranes, typically composed of thin films with a porous structure, have unique properties and functional capabilities that make them applicable to a wide range of solutions. The following papers [40]-[42] describe laboratory and pilot tests of multicomponent arsenic-containing solutions using a two-stage nanofiltration-reverse osmosis system. The conducted research has proved the high efficiency of water purification technology from highly mineralized and saline solutions containing micropollutants, including heavy metals.

The present research is devoted to the development of tailings solution purification technology using membrane nanofiltration at lead dust processing enterprises.

2. Research methods

2.1. Methodology for obtaining the initial solution for membrane filtration

This paper studies the composition of the initial solution and treated solutions obtained after purification with nanofiltration membranes. The initial solution is a tailings solution after gyrometallurgical processing of lead dust (Fig. 1).

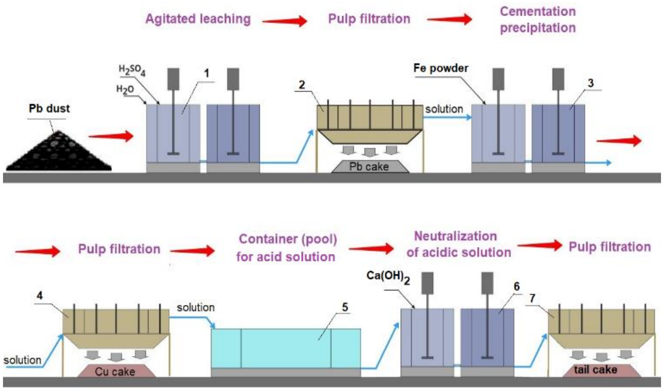

Figure 1. Lead dust processing technology: 1 – vat agitator for lead dust leaching; 2 – frame press filter for lead cake filtration; 3 – vat agitator for copper cementation; 4 – frame press filter for copper cake filtration; 5 – acidic tailings solution pool; 6 – vat agitator for acidic solution neutralization; 7 – frame press filter for tailings cake filtration

The technology for obtaining the initial solution includes sulphuric acid leaching of lead dust in vat agitators *1*. Afterwards, the pulp is sent to a frame filter press *2*, where a 50% lead concentrate and copper solution are obtained [43], [44]. The copper solution containing at least 20 g/l Cu is exposed to cementation precipitation in agitators *3* using iron powder to produce cementation copper. The pulp is then sent to a frame filter press *4* to obtain 75% copper concentrate and tailings solution. The tailings solution is sent to pool *5* for further neutralization of the acidic tailings solution. The tailings solution is neutralized in agitators *6*, using lime milk, thus producing a large amount of waste *7*, calcium arsenate, iron and zinc. The harmful and toxic compounds contained in the waste have a negative impact on the environment and are to be disposed of in special burial grounds. Construction and maintenance of burial grounds increases capital and operating costs of the enterprise, thereby increasing the cost of final product.

To reduce the volume of tailings solutions, with the subsequent possibility of obtaining additional metals and increasing the volume of recycled acidic liquors for leaching lead dust, the possibility of using membrane nanofiltration technology is studied. The purified acidic solution (permeate) with a residual sulphuric acid content of 3.5 g/l, pH – 2.9 can be returned to the initial stage of the process *1* – per leaching. At the same time, from products of nanofiltration – concentrated solution (retentate) of metals, it is possible to additionally extract zinc.

2.2. Analytical assessment of the initial solution using chemistry and thermodynamics

To determine the chemical composition of the studied ores, certified methods for determining As, Fe by titrametric method, Cu, Zn – by atomic absorption method, have been selected. Atomic-absorption analysis of samples for copper and zinc content is conducted in an AAS-1N atomic-adsorption spectrometer.

The main results of the experimental tests on purification of tailings solutions from impurities using membrane nanofiltration are given below. Table 1 shows the results of the initial solution chemical analysis.

Table 1. Results of the initial solution chemical analysis (tailings solution)

Name	Content, g/l						H_2SO_4	pH
	As^{3+}	AsO_4^{3-}	Zn^{2+}	Fe^{2+}	Fe^{3+}	Cu^{2+}		
Tailings solution	5.25	15.09	22.06	7.23	11.39	0.10	9.54	2.5

Chemical analysis of the initial solution shows the content of heavy metals and acid in the initial solution with impurities: As^{3+} – 5.25; AsO_4^{3-} – 15.09; Zn^{2+} – 22.06; Fe^{2+} – 7.23; Fe^{3+} – 11.39 g/l. Arsenic, iron, zinc content above 5 g/l in the recycled liquor has a negative impact when reused for the processes of hydrometallurgical processing of lead dust.

Figure 2 shows the Eh-pH diagram of a solution in the presence of metal ions of arsenic, iron, zinc and copper, which illustrates the stability fields of mineral or chemical particles in terms of hydrogen ion activity (pH) and electron activity (Eh).

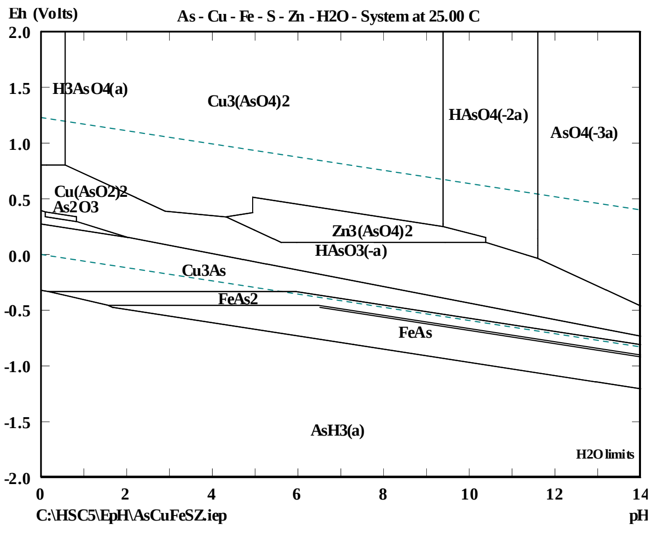

Figure 2. Eh-pH solution diagram in the presence of As, Fe, Zn and Cu

Figure 2 shows the Eh-pH diagram illustrating the thermodynamic behavior of a solution containing metal ions such as arsenic, iron, zinc and copper at 25°C. The diagram demonstrates the range of possible ions and compounds that can exist in the system. Eh values below 0.0 indicate a reduction potential, while values above represent an oxidation potential. In the presence of arsenic, iron, zinc and copper ions, the identification of a reduction potential leads to the formation of reduced oxygen-free compounds such as FeAs, $FeAs_2$, AsH_3 and Cu_3As. Conversely, when an oxidation potential is created by using different oxidizing components, various arsenate-ions of copper and zinc, arsenic and arsenious acids are formed. Also, the diagram indicates that the hydrolytic purification method cannot effectively remove arsenic ions due to the thermodynamic limitations of arsenic hydroxide formation in a wide pH range.

The dotted lines in the diagram represent the boundaries between the different types of equilibrium reactions in the system. At low pH, the system changes from an oxidation state of approximately 1.25 millivolts to a reduction state at 0.4 millivolts.

Moreover, the diagram shows that for effective arsenate-ion separation in combination with copper and zinc, it is necessary to maintain an oxidation potential above 0.5 millivolts and a pH – below 9.5. Given the different radii of metal-containing arsenate ions, arsenic and arsenious acids formed at pH above 9, information can be obtained that provides valuable guidance for selective separation by nanofiltration process [45].

2.3. Characterization of the equipment and membranes used

A semi-industrial nanofiltration pilot plant is used to conduct research on the technology of nanofiltration separation of tailings solutions from the lead dust processing enterprise. Structurally, the nanofiltration plant is a metal frame on which a low-pressure pump, a pre-filter with a 5 µm pore size for fine purification from mechanical suspended and foreign particles, nanofiltration membranes in housings, pressure gauges, rotameters and shut-off valves are installed. Stainless steel pipes are used for high-pressure areas. Polyvinyl chloride pipes are used for low pressure areas. The nanofiltration pilot plant is designed for concentrating and separating target initial solution components by filtering through membranes under pressure.

Nanofiltration membranes are thin polymer films with a dense structure and nanoporous surface. The pore size in such membranes is typically 1-5 µm, which allows high-molecular compounds, multiply charged ions and colloidal particles to be retained, but low-molecular ions and molecules to be passed through.

The main operating element of a nanofiltration plant is the membrane modules, consisting of housings capable of withstanding pressure up to 70 bar and the membranes themselves, connected to each other. The experiments on the nanofiltration unit use nanofiltration membranes from Dupont Company: "FilmTec" (NF 270 8040-34i). The main nanomembrane materials are polyamide (PA) and thin film composite (TFC). The performance characteristics of the nanomembranes used in the experiments are given in Table 2. Thus, the nanofiltration pilot plant is optimally configured to ensure efficient separation of tailings solution components.

Table 2. Operating parameters of nanomembranes used for experiments

No.	Parameter	Value
1	Membrane diameter	99 mm
2	Active membrane area	7.6 m^2
3	Maximum flow delivery rate	3.6 m^3/hour
4	Membrane length	1016 mm
5	Maximum pressure	4 MPa
6	Maximum temperature	40°C
7	pH range	2.5-3.0

The use of membranes with high strength and pressure resistance parameters enables reliable filtration processes in real production conditions. The obtained data can confirm the possibility of using this technology for effective purification and concentrating valuable components from industrial solutions, which contributes to resource saving and reducing the environmental burden caused by the enterprise.

2.4. Technological scheme of nanofiltration pilot plant

To increase the degree of retention of arsenic, zinc and iron, three membrane modules connected in series are installed during nanofiltration experiments of tailings solutions. The technological scheme of the nanofiltration pilot plant is presented in Figure 3.

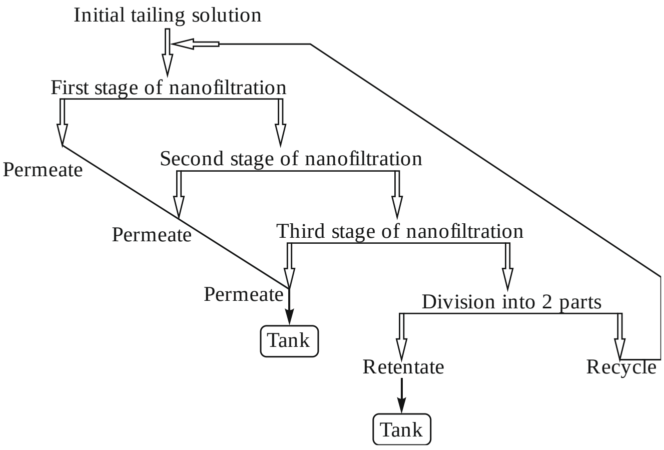

Figure 3. Technological scheme of the nanofiltration pilot plant

In accordance with the scheme, the initial solution passes successively three stages of nanofiltration, producing at each stage finished products – permeates and at the third stage – finished concentrate (retentate), one part of which – recycle is sent back to the 1st stage of nanofiltration. Permeate after the third nanofiltration stage and the resulting concentrate are sent to the appropriate containers.

2.5. Methodology of conducting experiments

The initial solution (Fig. 4) with a volume of 1 m^3 from container *1* flows by gravity into low-pressure pump *2* and under pressure is directed to the filter of fine purification *3* for purification from mechanical suspended and foreign particles. After the filter of fine filtration, the solution is fed to the high-pressure pump 4 and then to the membrane of the first nanofiltration stage. When the resulting solution passes through the membrane *5* of the first nanofiltration stage, it is separated into two solutions: solution passed through the membrane – permeate, and solution not passed through the membrane – concentrate.

Permeate from the first nanofiltration stage is combined with permeate from the second and third stages and is removed from the process and discharged into the permeate container *7*. The resulting concentrate of the first nanofiltration stage is fed to the second nanofiltration stage through the membrane *2* according to the technological scheme, and then to the third nanofiltration stage through the membrane *3*. The concentrate obtained at the third stage is separated into two parts.

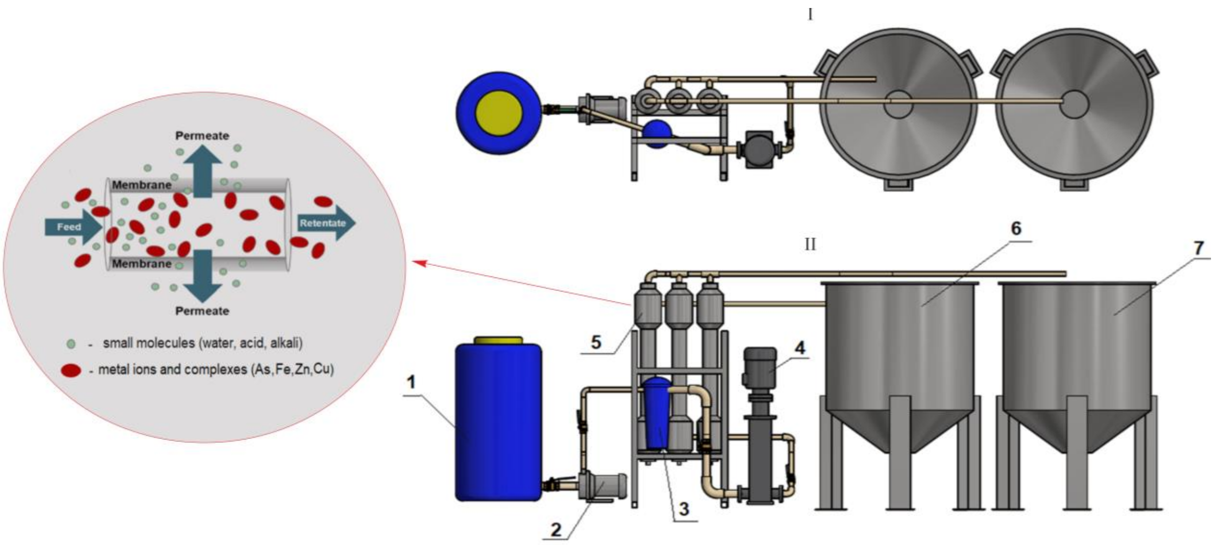

Figure 4. Membrane nanofiltration of tailings acidic solutions: I – top view; II – side view; 1 – initial solution container; 2 – low-pressure pump; 3 – filter of fine purification; 4 – high-pressure pump; 5 – membrane; 6 – concentrate container; 7 – permeate container

In accordance with the technological scheme, one part of the concentrate is fed to the concentrate container *6*, the other part is returned to the recycle and fed together with the initial solution to the first nanofiltration stage for further purification. The amount of combined permeate, third-stage concentrate and recycle produced is controlled by rotameter readings. The concentrate yield after the third stage and recycle (recycled concentrated solution or part of the concentrate) are set according to the rotameter readings and regulated by needle valves. The permeate yield is set by regulating the pressure in pumps *4* at the inlet to the membrane unit *5*.

3. Results and discussion

3.1. Mechanism of nanofiltration process of initial tailings solution

During the experiments, a decrease in the permeate yield and consequently a decrease in the specific membrane performance has been found. This decrease can be attributed to the phenomenon of polarization. It is known that all baromembrane processes are accompanied by polarization phenomena. This is due to the fact that different substances behave differently when concentrated: some may exceed the solubility limit and precipitate, some may form spatial grids and turn into a gel, and some may begin to accumulate on the membrane due to adsorption and surface forces (Fig. 5). In this case, the concentration of impurities has a significant influence on the performance of the membrane separation process. When the concentration of impurities in the solution increases, there is a decrease in the driving force and process rate, and there is an increase in the density and viscosity of the solution, which reduces the permeability value. This requires an increase in solution pressure and the time to process the solutions. Figure 5 shows additional resistance to mass transfer through the membrane.

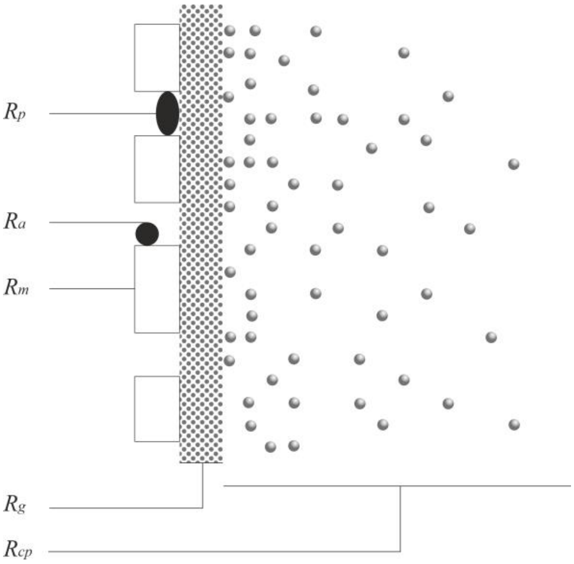

***Figure 5.** Different types of resistance to mass transfer through the membrane: (R_p – pore blockage; R_a – adsorption; R_m – membrane; R_g – gel layer; R_{cp} – layer of increased concentration of dissolved substances)*

The main separation mechanisms in nanofiltration are capillary-filtration and electrostatic mechanisms. As is known, the capillary-filtration mechanism of nanofiltration is based on the use of ultrathin pores with a diameter of several nanometres. These pores allow only molecules of a certain size to pass through, blocking larger particles. Capillary pressure plays a significant role in this process, as it involves the passage of liquid through narrow pores.

The electrostatic mechanism of nanofiltration is based on the use of charged membranes. Charged membranes attract and retain particles with a certain charge or charge opposite to the charge of the membrane. This mechanism works based on electrical forces and can be effective for removing particles of different size and charge from a liquid. In our case, the isoelectric point of the NF-270 membrane is in the range of pH = 3.3-4.0. Thus, at pH = 4 the membrane is negatively charged and at pH < 4 the membrane is positively charged. Consequently, at pH = 2.5 the membrane has a positive charge, thus the cation selectivity becomes high due to electrostatic repulsion. Thus, it can be assumed that the pH value is a determining factor influencing the efficiency of nanofiltration in the wastewater treatment from heavy metal ions. The negative charge of the membrane surface allows the retention of multivalent anions, as well as their associated cations, to maintain electroneutrality. Most divalent ions are retained by the membrane.

Sulphuric acid is dibasic and dissociates in solution in 2 stages: at the first stage, a monovalent bisulphate-ion and a hydrogen ion are formed:

$$H_2SO_4 « H^+ + HSO_4^- . \quad (1)$$

The bisulphate-ion is not retained by the membrane and passes through it, as does the chloride ion. At the second stage of dissociation, a divalent sulphate-ion is formed, but this requires a high concentration of sulphuric acid:

$$H_2SO_4 « 2H^+ + SO_4^{2-} . \quad (2)$$

The sulphate-ion is retained by the membrane, and those cations associated with the sulphate-ion will also be retained by the membrane and separated from the sulphuric acid. This allows for the concentration of metals and the extraction of sulphuric acid for reuse from weakly acidic solutions.

When the tailings solution passes through a nanofiltration membrane, the separation of solution components occurs under the action of applied pressure. Large metal ions such as As^{3+},AsO_4^{3-}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, having large sizes and high charges, are effectively retained by the membrane and concentrated in the retentate (concentrate). At the same time, small H^+ ions and H_2SO_4 molecules can partially pass through the membrane pores and be present in the permeate (purified solution).

3.2. Chemical analysis of the solution after nanofiltration

Experimental tests on purification of tailings solutions from heavy metals using a special nanofiltration plant include determining the dependence of harmful impurities content in permeate on the pressure injected into the membranes and solution temperature. The experiments performed on the pressure injected into the membranes provide for the determination of the degree of purification of tailings solutions with an increase of the permeate yield from 15 to 50% depending on the injected pressure of tailings solutions into the membranes from 2.5 to 4.0 MPa. Below are the results of experimental tests on the separation of heavy metal impurities from the tailings solution, depending on the pressure during the nanofiltration process and the yield ratio (Table 3).

***Table 3.** Results of chemical analysis of permeate depending on membrane nanofiltration pressure (temperature – 25 ± 2°C)*

Membrane pressure, MPa	Permeate yield, %	Content, g/l					
		As^{3+}	AsO_4^{3-}	Zn^{2+}	Fe^{2+}	Fe^{3+}	Cu^{2+}
2.5	15	0.24	5.45	6.61	0.01	0.98	0.023
3.0	20	0.35	5.97	7.20	0.02	1.08	0.021
3.5	30	0.48	5.83	6.95	0.03	0.77	0.018
4.0	50	1.40	8.86	9.67	0.10	4.39	0.020

Table 3 shows that when the nanofiltration pressure is increased from 2.5 to 4.0 MPa, the permeate yield increases from 20 to 50%, but the concentration of most metal ions in the permeate increases. This is explained by the fact that at higher pressure, more low-molecular ions and molecules, including metal ions pass through the membrane pores. However, at a pressure of 3.5 MPa, an optimal balance between performance and selectivity is achieved, ensuring a high degree of solution purification. Efficient purification is achieved at a pressure of 3.5 MPa, while the As^{3+} content in the permeate decreases from 5.25 to 0.48 g/l, AsO_4^{3-} – from 15.09 to 5.83 g/l.

Table 4 shows the dependence of purification degree on temperature increase during the process of membrane nanofiltration of solutions. Experiments include determining the degree of tailings solution purification when the tailings solution temperature is increased from 25.0 to 35°C at a stable pressure in the membranes of 35 MPa.

Table 4. Results of chemical composition analysis of solutions depending on increasing temperature of membrane nanofiltration (pressure – 3.5 MPa)

Temperature, °C	Content, g/l					
	As^{3+}	AsO_4^{3-}	Zn^{2+}	Fe^{2+}	Fe^{3+}	Cu^{2+}
25 ± 2	0.48	5.83	6.95	0.03	0.77	0.018
30 ± 2	0.81	8.02	8.70	0.09	2.08	0.041
35 ± 2	0.28	12.43	8.45	0.11	6.79	0.084

Table 4 shows that when the temperature is increased from 25 to 35°C, the AsO_4^{3-} content increases from 5.83 to 12.43. The data analysis shows that when temperature is increased from 25 to 35°C at a pressure of 3.5 MPa, the concentrations of metal ions in the permeate increase. This is due to the fact that when the temperature of the solution increases, more dissolved substances, including metal ions, pass through the membrane. The optimal mode in terms of purification quality is the process temperature – 25 ± 2°C, pressure in membranes – 3.5 MPa.

Thus, the mechanism of tailings solution nanofiltration is based on the differences in size and charge of the ions and molecules present, as well as on selective properties of nanofiltration membranes that retain large multiply charged heavy metal ions but allow low-molecular ions and molecules to pass through. Varying the process parameters (pressure and permeate yield) allows optimizing solution purification degree and obtaining concentrated metal solution (retentate) and purified acidic solution (permeate). Also, the increase of arsenic content in permeate is described in detail in the paper [46].

3.3. Comparative characterization of solutions before and after nanofiltration

Figure 6 clearly illustrates the efficiency of solution separation using membrane nanofiltration – permeate is a transparent solution with low metal content, and the concentrate is a turbid solution with high metal concentrations.

(a) (b)

Figure 6. Solutions obtained after the membrane nanofiltration process: (a) permeate; (b) concentrate

A comparative analysis of the results after membrane nanofiltration of tailings solutions is presented below (Table 5).

Table 5 demonstrates the effectiveness of membrane nanofiltration in the separation of heavy metals and acid. A significant reduction in heavy metal concentrations is achieved in the permeate (purified solution): As^{3+} – by 90.9%, AsO_4^{3-} – by 61.3%, Zn^{2+} – by 68.5%, Fe^{2+} – by 99.5%, Fe^{3+} – by 93.2%, Cu^{2+} – by 82%, compared to the initial solution. In this case, the H_2SO_4 concentration decreases slightly from 9.55 to 3.02 g/l, which allows the use of the purified solution as recycled liquor at the leaching stage.

Table 5. Comparative analysis of results before and after membrane nanofiltration of tailings solutions at optimal process parameters (pressure (const) – 3.5 MPa, yield (const) – 30%, temperature – 25 ± 2 °C)

Name	Content, g/l						H_2SO_4	pH
	As^{3+}	AsO_4^{3-}	Zn^{2+}	Fe^{2+}	Fe^{3+}	Cu^{2+}		
Initial solution								
Tailings solutions, g/l	5.25	15.09	22.06	7.23	11.39	0.10	9.54	2.50
Metal content in membrane nanofiltration products, g/l								
Permeate (purified acidic solution)	0.48	5.83	6.95	0.03	0.77	0.018	3.50	2.90
Retentate (concentrated acidic solution)	5.11	15.34	21.46	9.29	11.87	0.098	7.54	2.60
Metal content in membrane nanofiltration products, %								
Permeate	9.1	38.7	31.5	0.5	6.8	18.0	–	–
Retentate	97.4	101.7	97.3	128.5	104.2	98.0	–	–

The concentrate, on the contrary, has a high content of most metal ions, increased compared to the initial solution: AsO_4^{3-} – by 1.7%, Fe^{2+} – by 28.5%, Fe^{3+} – by 4.2%, and there is also a slight decrease in ions of Zn^{2+} by 2.7%. This opens up the possibility of additional extraction of metals such as zinc from the concentrate.

The efficiency of the membrane process is mainly determined by the properties of the membranes used. The main characteristics of membranes are specific performance, selectivity, as well as their chemical resistance in different solutions at different pH values.

The difference in membrane throughput capacity for different substances leads to their redistribution between permeate and retentate, and changes in their concentrations, which is the main purpose of membrane filtration. To characterize membrane throughput capacity, the term "selectivity" φ (retention coefficient) for separating components is used, determined as follows:

$$\varphi = \left(1 - \frac{C_2}{C_1}\right), \quad (3)$$

where:

C_1 – the concentration of dissolved substance in concentrate-retentate;

C_2 – the concentration of dissolved substance in permeate.

In the case, when $\varphi = 1$, it means that the component concentration in permeate is 0, that is, the component remains completely in the concentrate. If $\varphi = 0$, the component concentrations in the concentrate and permeate are equal, that is, the component "does not notice" the membrane. The specific membrane performance at constant pressure is characterized by the volume of filtrate (permeate) passing per unit time through surface unit and is proportional to the difference of applied and osmotic pressure:

$$q = \frac{Q_n}{S \cdot \tau} = k\left(p - \Delta\pi\right), \text{ ml/cm}^2\text{/min}, \quad (4)$$

where:

Q_n – the filtrate volume flow rate;

S – the membrane surface;

τ – the separation time;

k – the membrane permeability coefficient;

p – the applied pressure;

$\Delta\pi$ – the difference in osmotic pressures of solutions on both sides of the membrane.

Concentration factor (K) is determined as the ratio of the initial solution volume (V_i) to the concentrate volume (V_r):

$$K = \frac{V_i}{V_r}. \quad (5)$$

Conversion (C) is expressed as a percentage of permeate yield from the initial solution flow rate:

$$C = \frac{Q_n}{Q_i} \cdot 100\%, \quad (6)$$

where:

Q_n – the filtrate (permeate) volume flow rate, m^3/h;

Q_i – the initial solution volume flow rate, m^3/h.

Thus, the research results have shown that the use of membrane nanofiltration at optimal parameters (pressure 3.5 MPa, permeate yield 30%, temperature 25 ± 2°C) makes it possible to achieve a high degree of purification of tailings solutions from heavy metal ions to produce a purified acidic solution suitable for reuse, as well as concentrated metal solution for further extraction of valuable components. The developed technology is resource-saving and environmentally friendly.

4. Conclusions

Experimental tests on purification of tailings solutions from impurities of heavy metals (iron, arsenic and zinc) have shown positive results and possibility of using membrane nanofiltration technology. Effective nanofiltration process parameters have been developed to achieve a high degree of tailings solution purification from polluting impurities, ranging from 69.0 to 95.7%. It has been determined that effective removal of heavy metal ions (arsenic, zinc, iron) is achieved at a pressure of 3.5 MPa in nanofiltration membranes with a pore size of 1-5 μm: As^{3+} from 5.25 to 0.48 g/l; AsO_4^{3-} from 15.09 to 5.83 g/l; Zn^{2+} from 22.06 to 6.95 g/l; Fe^{2+} from 7.23 to 0.03 g/l; Fe^{3+} from 11.39 to 0.77 g/l. In this case, a concentrated metal solution is formed with the content of As^{3+} – 5.11 g/l; AsO_4^{3-} – 15.34 g/l; Zn^{2+} – 21.46 g/l; Fe^{2+} – 9.29 g/l; Fe^{3+} – 11.87 g/l, as well as purified acidic solution – permeate with a residual sulphuric acid concentration of about 3 g/l.

Comparative analysis of the degree of tailings solution purification from heavy metal ions has shown the following results: from arsenic – 69%, zinc – 68.5%, iron – 95.7%. The high degree of purification is achieved by efficient retention of heavy metal ions by nanofiltration membranes when the solution passes under pressure.

The zinc content in the concentrate has decreased insignificantly compared to the initial tailings solution, opening up prospects for further extraction of this metal.

The use of membrane nanofiltration can reduce the waste volume by 30% by purifying the tailings solution and reducing the tailings solution when processing lead dust. The purified acidic solution with a residual sulphuric acid concentration of about 3 g/l can be returned to the beginning of the process for reuse when leaching lead dust, thereby reducing the consumption of fresh sulphuric acid and water by 10-15%. Technical and economic calculations have shown that the implementation of the developed technology for tailings solutions purification using membrane nanofiltration will reduce the processing costs by reusing the purified water, additional zinc extraction from the concentrate and a significant reduction in the volume of waste requiring disposal.

Thus, the research results have demonstrated high efficiency and promising application of membrane nanofiltration for purification of tailing solutions generated during the processing of lead arsenious dust. The developed technology for tailings solution purification is resource-saving and environmentally friendly, reduces the volume of waste, reuses purified water and additionally extracts valuable components.

Author contributions

Conceptualization: BA; Data curation: NT; Formal analysis: AL; Investigation: BA, AL; Methodology: AK; Project administration: BA, ZT; Resources: ZT; Software: AK; Supervision: ZK; Validation: OB; Visualization: OB; Writing – original draft: NT; Writing – review & editing: ZK. All authors have read and agreed to the published version of the manuscript.

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Conflicts of interests

The authors declare no conflict of interest.

Data availability statement

The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

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Дослідження очищення хвостових розчинів підприємств з переробки свинцевого пилу від домішок металів

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Мета. Розробити технологію очищення хвостових розчинів із застосуванням мембранної нанофільтрації для зменшення обсягу відходів та зниження витрат підприємства за рахунок повторного використання очищеної води.

Методика. У дослідженні застосовувалися нанофільтраційні поліамідні мембрани на напівпромисловій установці. Процес нанофільтрації проводився при тиску 3.5 МПа з виходом пермеату 30%. Аналіз хімічного складу розчинів здійснювався атомно-абсорбційними та хімічними методами.

Результати. В оптимальних умовах досягнуто видалення 69% миш'яку, 68.5% цинку та 95.7% заліза. Очищений розчин із залишковою концентрацією сірчаної кислоти ~3.5 г/л може бути повторно використаний для вилуговування свинцевого пилу. Концентрований розчин металів дозволяє додатково отримувати цинк. Застосування даної технології дає змогу скоротити обсяги відходів більш, ніж на 30% та знизити витрати підприємства на переробку.

Наукова новизна. Дослідження пропонує нову екологічно безпечну технологію нанофільтрації для очищення хвостових розчинів, яка дозволяє ефективно видаляти важкі метали та відновлювати цінні компоненти. Даний підхід унікальний використанням мембранної нанофільтрації при оптимізованому тиску 3.5 МПа, що забезпечує високий рівень видалення іонів важких металів, таких як As^{3+}, AsO_4^{3-}, Zn^{2+}, Fe^{2+} та Fe^{3+}, скорочення обсягу відходів на 30%, а також повторне використання сірчаної кислоти і води в процесі вилуговування, що веде до значної економії ресурсів та зниження витрат.

Практична значимість. Впровадження запропонованої технології на підприємствах переробки свинцевого пилу знижує витрати на очищення стічних вод, зменшує обсяг відходів та дозволяє повторно використовувати воду й кислоти у виробничому процесі.

Ключові слова: *мембранна нанофільтрація, важкі метали, очищення стічних вод, свинцевий пил, ресурсозбереження, вилучення цінних компонентів*

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