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DEVELOPMENT OF METAL EXTRACTION TECHNOLOGY FROM ABANDONED MINE WASTEWATER

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Annotation. One of the most important environmental tasks is the treatment of wastewater from enterprises in various industrial sectors. Technologies for treating wastewater containing heavy metals allow for the creation of water treatment and water circulation systems for many industrial facilities. One of the processes for treating wastewater is ion flotation.

The process of ionic flotation depends on many physical and chemical factors, such as the type and concentration of the foam-forming agent and aggregate,

flotation time, the ionic force of the treated solutions, and the nature of the metal ions being extracted. Since these factors are interconnected, controlling the ion flotation process is quite difficult to find their optimal correlation. Therefore, an important trend in ion flotation research is the search for conditions that increase the efficiency of conducting the process to the maximum possible extraction of metals with minimal agent consumption.

PREFACE

Relevance of the scientific project. The pollution of the environment, which is the primary source of water systems, is one of the most significant environmental issues of our time. Multiple texnogenic water streams contain heavy metals that possess high toxicity and stability in the environment. Therefore, the removal of heavy metals from various types of industrial waters is a pressing task, as evidenced by numerous studies conducted in this field in recent years.

In recent years, there has been a sharp increase in the number of cases involving such an advanced method for extracting heavy metals from technogenic solutions as ion flotation. The main advantages of ion flotation are: simplicity and efficiency, low energy intensity, low residual metal concentration, high process speed, small device sizes, ease of applying the method to different metals at different levels, and the production of a small volume of waste [1-3].

The aim of the conducted research is to analyze modern trends in the development of ion flotation theory and practice as a fundamental technology for purifying technogenic waters.

Purpose of this project: Development of technology for cleaning wastewater from abandoned quarry solutions and extracting metals.

Tasks:

- study literature;
- determining the concentration of metal ions within abandoned quarry solutions;
- development of parameters for the ion flotation process;
- analyze the results obtained.

The object of the study is wastewater from an abandoned mine—the Kurgashinkan mine.

Methods: when conducting research (measurement, experiment, comparison, observation, analysis).

LITERATURE REVIEW

Research on wastewater treatment with ozone. One of the "ecologically clean" technologies for extracting metals from cleaning solutions is the technology of cleaning using ozone [4]. Ozonation includes both oxidation processes of organic and inorganic compounds or neutralization with dissolved ozone in water, as well as oxidative processes occurring with the participation of hydroxyl radicals formed as a result of chemical transformations of ozone. Ozone is one of the strongest natural oxidizing agents. The interaction of compounds with ozone is characterized by multi-stage transformations with the formation of intermediate products that have different reactivity relative to the oxidizers involved in the process.

The oxidizing properties of ozone in water can manifest in direct oxidation, catalysis, radical oxidation, and polymerization reactions [5]. Some organic compounds undergo direct oxidation. The action of ozone on water impurities can manifest in the following forms: direct oxidation, indirect oxidation (oxidation by active radicals), ozone oxidation, and catalysis. Direct reactions of oxidation of dissolved substances by ozone are described by a simplified scheme: [substance] + [O_3] - [oxide of the substance] + [O_2].

Ozone is one of the strongest natural oxidizing agents. Its oxidation-reduction potential (2.07 V) is second only to that of fluorine (2.8 V) and OH radicals (2.38 V). It is also a strong disinfectant agent [6].

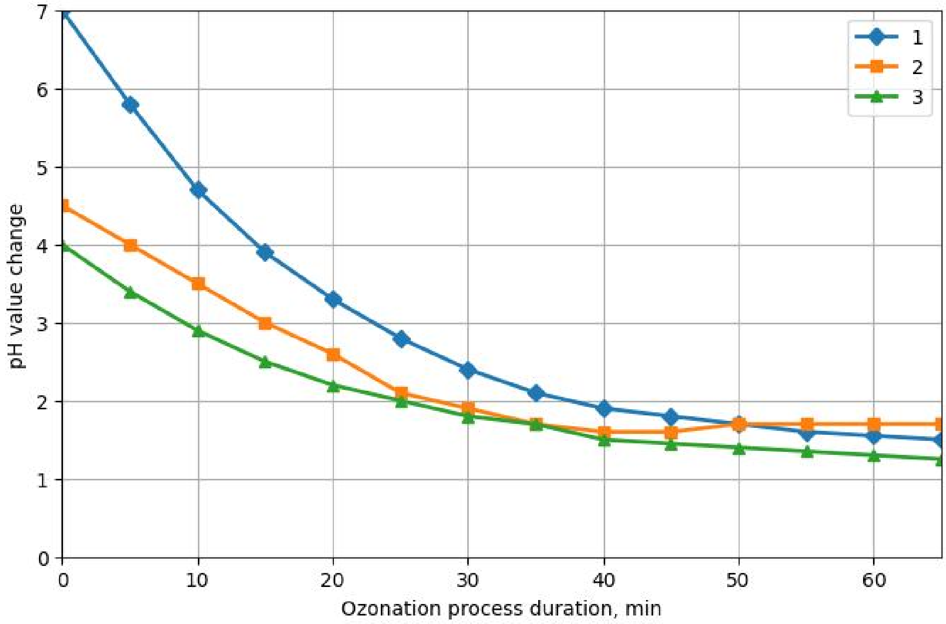

Figure 1. Changes in the pH of various types of water during ozonization: 1-ordinary water; 2- acids; 3-washing solutions.

Thus, the main advantages of ozonization can be noted. Ozone kills all known microorganisms 300-3000 times faster than any other disinfectant, acts very quickly - within a few seconds, removes unpleasant odors and taste, is produced on the spot, does not require storage and transportation, does not change the pH of the water. The studies were conducted using ordinary water (pH -7.2) and wastewater from copper and zinc production (acidic wastewater from the sulfate workshop and washing solutions from the sulfuric acid workshop). An ozone-air mixture with an ozone concentration of 2.5 mg/l, obtained from dried air in an ozonator, was used as the ozone-containing gas. The experiments were conducted at a temperature of 21±1°C, with a gas mixture flow rate of 500 ml/min. After ozonation for 15, 30, 45, 60, and 75 minutes, samples were taken and analyzed for metal content. The process was accompanied by the formation of a precipitate (metals and non-metals). When studying the change in pH of various types of water during ozonization, it was established that within 40 minutes, the pH of all water samples decreased to values of 1.5–1.8 (Fig. 1) [7].

The interaction of ozone with wastewater depends on the type of pollutant and heavy non-ferrous metal ions. The consumption of ozone per 1 mg of metal ions depends on the degree of wastewater pollution and the duration of their contact with the ozone-air mixture. The decomposition of ozone in water at different temperatures is shown in Figure 2.

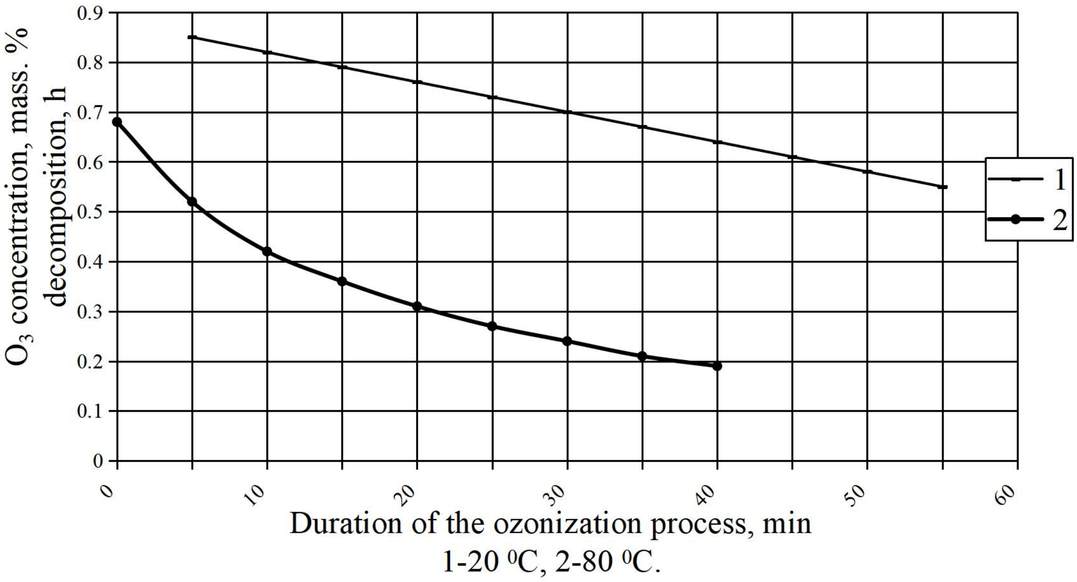

Fig. 2. Dependence of ozone concentration (decomposition) in water on the duration of the ozonation process at various temperatures

Cleaning wastewater using the ozonization method involves the most complete neutralization of a wide range of metal-containing complex compounds that are part of the generated wastewater. Ozone production is carried out directly at the site of consumption. Due to its high oxidizing potential, ozone effectively oxidizes all metal-containing compounds, with the exception of iron complex compounds, the precipitation of which can be carried out with the further use of iron sulfate. Ozonation is widely used for wastewater treatment, primarily for disinfection and sterilization purposes[8].

The disadvantages of ozonization include: the high cost of the ozonator, which grows in geometric progression depending on productivity; the need for special air preparation (drying) or oxygen operation; the insufficient ability of ozone to break down phenolic compounds; the need for long-term contact between ozone and the pollutant in the case of complex compounds; ozone is a toxic gas, so any use of it requires thorough safety control; due to the saturation of water with an ozone-air mixture, it acquires high oxidizing capacity and becomes corrosive-active, requiring the use of special equipment and materials; and the short duration of action due to the fact that ozone decomposes quickly in water. It should also be noted that with a relatively high cost of primary capital expenditures, operational costs are associated only with electricity consumption (averaging 0.05–0.07 kW per 1 g of ozone). Thus, the conducted literature review shows that using ozonization for water purification is a highly promising method [9].

Investigation of the dependence of metal extraction from solutions using the ion flotation method. The flotation of ions and molecules underlies four related processes. In all these processes, the gas is barbed through the solution layer, and the emerging bubbles adsorb the sublate and transport it to the solution surface. The difference between the specified processes lies primarily in the method of separating the sublate concentrated on the surface of the bubbles. In foam separation (English: foam separation), the emerging bubbles form a relatively stable foam in which the sublate accumulates. Foam usually flows out of the apparatus spontaneously and, after destruction, forms a top (enriched or foamy) product. Both periodic and continuous processes are possible. In the latter case, the initial solution is supplied below the foam level or above it by a fraction of the foam.

The extraction of various substance ions from weak aqueous solutions by flotation is called ionic flotation. The term "ion flotation" was introduced in 1959 by Felix Sebba, a professor of physical chemistry at the University of Witwatersrand (South Africa, Johannesburg), to denote the flotation process intended for extracting ions from a solution. As collecting reagents during ion flotation, substances with high surface activity (SPA) are used.

For ion flotation, it is necessary that the corresponding ion can be concentrated at the "liquid-gas" phase boundary, i.e., on gas bubbles passing through the solution. The process conditions are selected in such a way that the gas bubbles barbed through the solution float the compound (sublate) of the extracted ion (collagen) with the surfactant, and a small (no more than a few centimeters) layer of unstable foam forms on the surface of the solution, in the upper layers of which, as a result of secondary concentration processes, so-called foam (solid hydrophobic product) is formed, accumulating the sublate [11].

The characteristic features of ion flotation that distinguish it from related processes are the use of SFM as collectors and the presence of foam.

According to A.N. Frumkin and A.V. Gorodetskaya [4], the outer surface of the bubbles is negatively charged, and cations are concentrated in the outer lining of the double layer on the bubbles in the foam. In the solution captured by the bubbles, the concentration of cations will be higher than in the original solution when the foam is destroyed. However, this process is ineffective.

The efficiency of the process increases sharply if a collector—a heteropolar organic substance that forms a strong compound with ion extraction—is added to the solution.

For cation flotation, an anion-type collector is required, for example, R–COO- (carboxylate), R–SO-3 (sulfonate), R–OSO-3 (sulfate), RC_6H_5–SO-3 (benzosulfate), R–OPO_2-3 (phosphate), R–$CHSO_3COO$- (sulfocarboxylate), where R is the hydrocarbon radical CnH_{2n}+1; n=10-16. For anion flotation, cation-type collectors are used, for example, R–NH_2 (primary amine); secondary R_2NH; tertiary R_3N.

It should be emphasized that nowadays, with the correct choice of reagent regime, ion flotation allows for extracting 90-99% of the metal contained in a solution with an initial concentration of tens to hundreds of milligrams per liter within a few minutes, with SFM losses at a level of several milligrams per liter, and obtaining a foam product with a moisture content of 10-20%. Meanwhile, the industrial development of ion flotation and the associated detailed research of the process are only just beginning, so it seems there are significant reserves for increasing the efficiency of this process.

An analysis of the reviewed literature and the practice of operating enterprises on the problem of processing metal extraction from metal-containing wastewater allows for the following conclusions:

1. Most enterprises use various methods to extract metals from solutions and wastewater. All research work to improve the process was aimed at finding new, affordable, and inexpensive reagents, and certain successes have been achieved in this direction. However, numerous methods are insufficiently effective and do not allow for the complete removal of metals from the product.

2. Ion flotation and ozonization are promising methods for extracting substances from solutions. The possibility of applying ion flotation to solutions containing metals is of interest.

3. As a result of literature analysis, the necessity of creating an effective technology for the selective extraction of metals from the wastewater of the abandoned mine—the Kurgashinkan mine—has been demonstrated.

To achieve this, it is necessary to conduct scientific research in the following areas:

1. Study the possibility of extracting metals from solutions using ion flotation and ozonization methods, and develop process parameters;

3. Develop a fundamental technology for extracting metals from the wastewater of the abandoned mine - Kurgashinkan Mine.

MATERIALS AND METHODS.

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Research objects: The Kurgashinkan mine is the oldest mining enterprise of the plant, which began its operations in 1931. Main useful components: lead, zinc; associated: gold, silver, copper, cadmium, bismuth, and a number of other rare-earth elements. In 1951, the deposit was assessed as industrial and a mine was established. Subsequently, the southwestern Kurgashinkan and Kulkermes deposits were explored, and a "contact deposit" was discovered.

The Kurgashi mine produced ore for 43 years. Its operation was suspended in 1994, and the quarry was mothballed. And then it was flooded by groundwater with a volume of about 20 million cubic meters.

Figure 3. Sampling process from the "Kurgashinkan" mine

Table 1. Results of chemical analysis of the Kurgashinkan quarry

2.2. Research Methods

The diagram of the laboratory unit and the operating principle of the wastewater ozonation process for abandoned quarry solutions are shown in Figure

Table 1

Chemical composition of water

No.	**Parameter**	**Symbol**	**Standard, mg/L**	**Sample No.**
1	Potassium	K	Not regulated	11.5
2	Sodium	Na	Not regulated	332
3	Ammonium	NH_4	Not regulated	Not detected
4	Calcium	Ca	Not regulated	605
5	Magnesium	Mg	Not regulated	342
6	Iron	Fe	0.3	0.0087
7	Chlorides	Cl	250 (350)	269.8
8	Sulfates	SO_4	400 (500)	2990.61
9	Nitrites	NO_2	3.0	0.045
10	Nitrates	NO_3	45.0	11.81
11	Bicarbonates	HCO_3	Not regulated	217.16
12	pH	—	6–9	6.96
13	COD (Chemical Oxygen Demand)	—	Not regulated	24
14	Total Dissolved Solids (Dry Residue)	—	1000 (1500)	4704
15	Copper	Cu	1.0	0.0383
16	Zinc	Zn	3.0	6.20
17	Lead	Pb	0.03	0.0107
18	Molybdenum	Mo	0.25	0.0035
19	Arsenic	As	0.05	0.0011

20	Cadmium	Cd	0.001	0.0200
21	Manganese	Mn	0.1	0.271
22	Chromium	Cr	0.05	0.0022
23	Aluminum	Al	0.2 (0.5)	0.0256

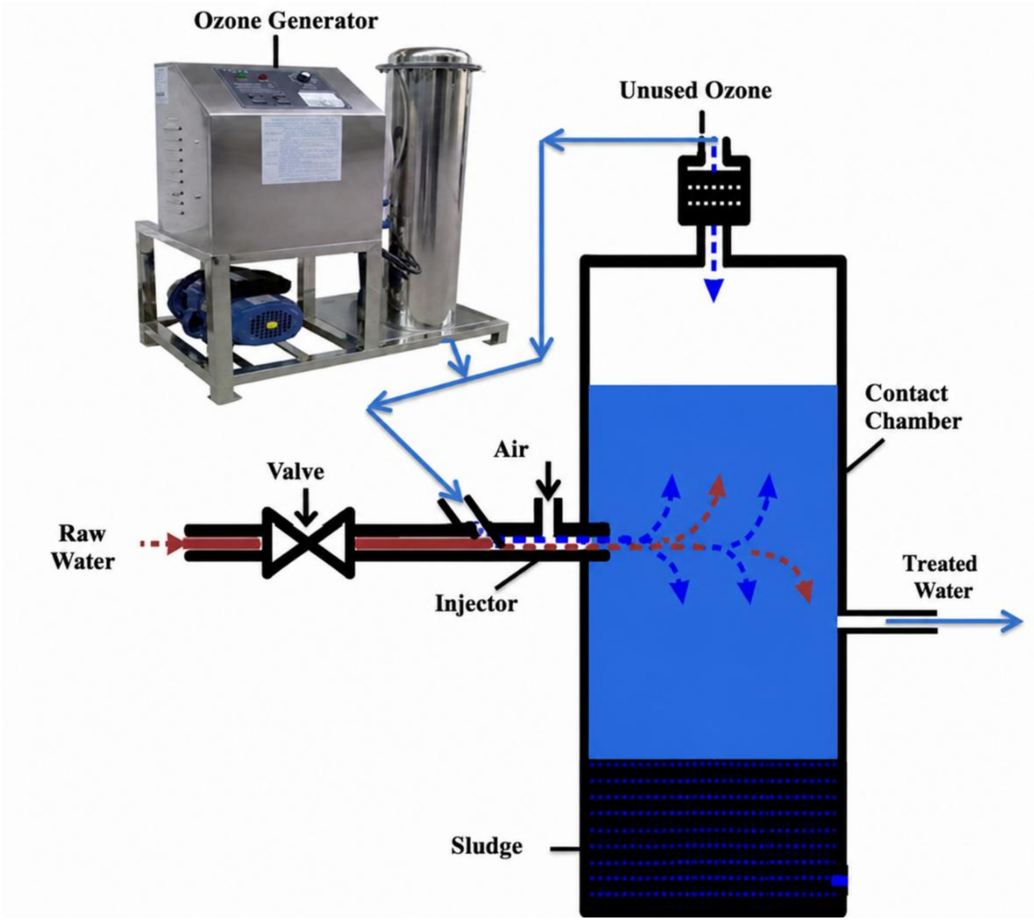

Figure 4. Diagram of a laboratory installation for treating wastewater from abandoned quarry solutions

EXPERIMENTAL PART.

Experiments on studying wastewater treatment. Experiments to study the influence of the initial pH value of the environment on the intensity of wastewater treatment at the abandoned mine—the Kurgashinkan mine—showed that the oxidation of impurities by both ozone-air mixtures and air oxygen proceeds intensively for the first 15 minutes in almost all cases. Then the oxidation rate is reduced. The ozonator's productivity is 3 g/h. In the experiments, 1–1.5 g of ozone was used for 10 liters of technological solution.

The maximum purification of wastewater from the abandoned mine—the Kurgashinkan mine—in an acidic environment can be explained by a chemical process accompanied by the enlargement of ion molecules (reactions of hydroxyl and peroxide radicals with high oxidation potential values) and the formation of sediment, which is confirmed by the amount of solid fine-dispersed phase formed.

The oxidation intensity of wastewater from the abandoned mine—the Kurgashinkan mine—increases with increasing temperature (Fig. 5), but with a duration of 70-80 minutes, the degree of wastewater purification is the same regardless of the temperature increase.

Within ten to twenty minutes, the interaction of ozone with easily oxidizing substances in wastewater occurs. However, as seen in Figure 5, the impurity content significantly decreases after an hour of treatment, then stabilizes. It can be assumed that during the ozonation process, not only surface oxidation of metals occurs but also the formation of peroxides, which, by diffusion, penetrate into the depths of the particles and cause secondary oxidative processes.

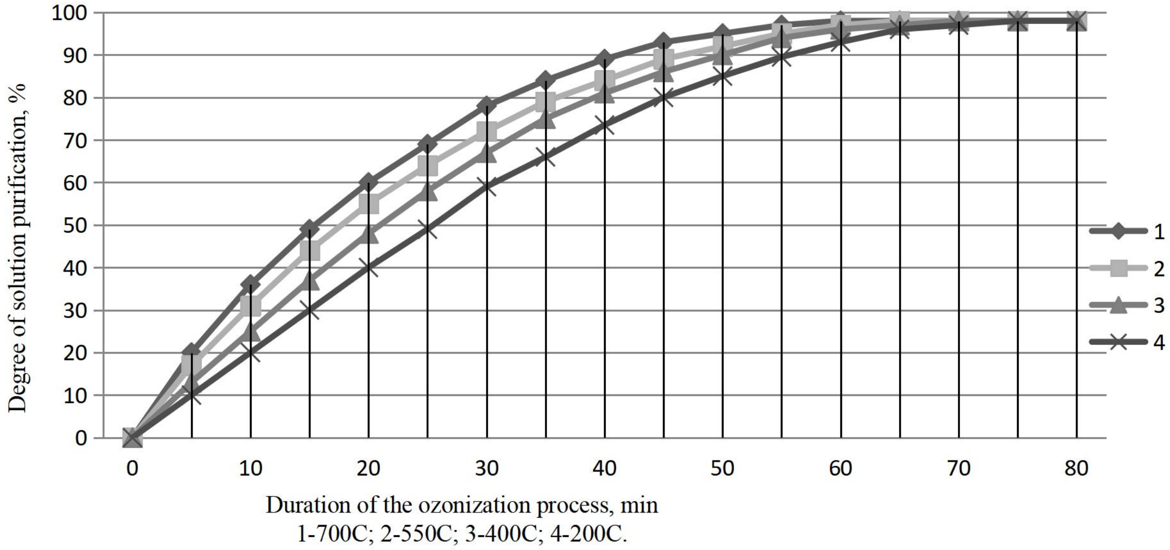

Figure 5. Dependence of purification degree change on ozonization time and temperature

Assembly of equipment for enlarged laboratory tests. Ozonation of wastewater is a process of absorption accompanied by an irreversible chemical reaction in the liquid phase. Due to the chemical reaction, the driving force increases, and the process proceeds faster than in the case of simple physical absorption.

To increase the process speed in the diffusion region, it is necessary to increase the contact surface of the phases. Increasing pressure is also effective for the absorption process.

The scheme for introducing the ozone-air mixture is recommended for removing impurities from wastewater that react with ozone quite quickly (Fig. 6). Such a scheme is accompanied by the formation of gaseous products that require separation from the air; furthermore, ozone is not fully utilized in it.

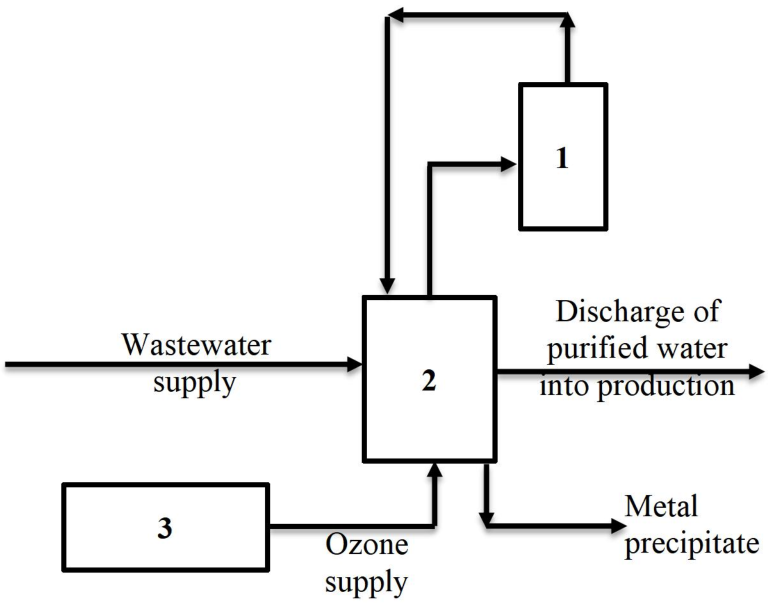

Figure 6. Ozonation plant diagram for copper and zinc production wastewater. 1-exhaust gas collector; 2-contact chamber; 3-device for obtaining ozone

Wastewater after ozonization qualitatively meets the requirements of the MPC due to achieving a high degree of water purification (up to 99%) from metal cations of copper, zinc, iron, nickel, lead, cadmium, etc. (Table. 2).

Table 2. Concentration of metals in wastewater and after the ozonization process, and comparison with the MPC

Parameter	Wastewater Concentration (mg/L)	After Ozonation (mg/L)	MPC (mg/L)	GOST 9.314, Category 2 (mg/L)
Copper, Cu^{2+}	5–30	< 0.04	0.004	0.3
Nickel, Ni^{2+}	5–30	< 0.01	–	1.0
Zinc, Zn^{2+}	5–30	< 0.01	0.03	1.5
Chromium, Cr^{3+}	5–30	< 0.01	0.4	0.5
Iron, Fe^{3+}	5–30	< 0.01	0.4	0.1
Aluminum, Al^{3+}	5–30	< 0.01	–	(0.5)
Lead, Pb	5–30	< 0.01	0.06	(0.03)
Cadmium, Cd^{2+}	5–30	< 0.04	0.003	0.01
Sulfates, SO_4^{2-}	800–1000	< 30	100	50
Chlorides, Cl	100–200	< 4	300	35
Surfactants (SAA)	1–5	< 0.01	0.9	1.0
Petroleum Products	5–30	< 0.01	0.3	0.3

The final product of the proposed technology is directed to existing processing schemes of a non-ferrous metallurgical enterprise for the production of marketable products.

CONCLUSION.

Based on the conducted research, the following conclusions were drawn:

1. It has been established that the ozonation process has significant advantages over other wastewater treatment methods.

2. Ozonation can be used to remove salts of a number of heavy metals: metal sulfates, carbonates, etc., from the wastewater of an abandoned mine. It was established that within 1 hour of treatment, the concentration of metals (Fe, Zn, Cu) decreased to a level of <0.01 mg/l, which is an order of magnitude lower than the MPC for metals in water, and also reduces environmental damage.

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