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APPLICATION OF OZONE FOR THE TREATMENT OF PROCESS SOLUTIONS AND WASTEWATER IN COPPER PRODUCTION

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Abstract - The issue of processing and rational use of natural resources is closely linked to the efficiency of industrial production, environmental protection, and new developments in the field of industrial waste recycling. The utilization of this waste is an important task for preventing environmental pollution. Ozonation is a promising method for treating process solutions and wastewater containing metals. Under the influence of ozone, the chemical composition of the precipitated metals changes. Sulfate compounds of metals present in the process solution decompose into metal ions and acidic residues, and the metal ions interact with hydroxide ions (OH^-) to form metal precipitates. Ozonation can be used to remove salts of several heavy metals from process solutions, such as sulfates and carbonates of metals. It has been established that after one hour of treatment, the concentration of metals (Fe, Zn, Cu) decreases to a level of less than 0.01 mg/l, which is an order of magnitude below the maximum permissible concentration (MPC) of metals.

Keywords: Ozonation, Treatment, Solution, Copper, Chemical composition, Reactor, Solid phase.

1. Introduction

Currently, large amounts of various wastes have accumulated in the areas of metallurgical complexes, with volumes reaching several million tons. Solid metallurgical wastes are primarily categorized as high-tonnage, making their processing an increasingly urgent issue due to the diminishing availability of storage space. Given the significant concentrations of harmful impurities (especially zinc, lead, potassium, sodium, etc.) in the wastes, additional measures for their treatment prior to disposal are required. An analysis of known methods and waste management practices at various enterprises shows that the primary trend is to process wastes at dedicated facilities. Since multiple processing technologies and equipment types are usually available for each type of waste, the number of proposed solutions is excessively large. This complicates the economically sound selection of a specific technology and fragments the unified issue of industrial waste utilization into separate parts. Based on an analysis of the current situation, a concept has been developed that significantly enhances the efficiency of waste processing.

The work mentioned below examines the environmental hazards associated with the mining and metallurgical sectors. It examines issues brought on by soil, water, and air pollution and offers fresh approaches to potential solutions. Specifically, exothermic self-propagating high-temperature synthesis of solid-phase recovery of metals (SHS) and phytoremediation are highlighted as examples of such novel and energy-efficient methods. There are visual proofs of the effectiveness of the chosen techniques. Compared to the previous approaches, the suggested technologies to address the ecological issues brought on by the mining and metallurgical industries are 20–30 times more affordable, straightforward, and environmentally safe. These techniques not only offer creative, energy-efficient ways to recover and recycle valuable materials, but they also open up new avenues for production that is waste-free globally. A metallurgical plant's location must take into account a number of considerations, including government laws, economics, and the availability of labor, raw materials, and power. Two additional factors are becoming more and more crucial to take into account: Environmental pollution and energy efficiency [1].

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Wastewater treated with lime typically has an alkaline pH, which enhances ozone's oxidizing ability, allowing many organic substances to break down into low-molecular-weight oxidation products, sometimes leading to complete mineralization. The presence of heavy metal ions in the water can catalytically accelerate the ozone oxidation process of organic substances [2-3].

The disadvantage of ozonation is the high cost of the ozone generator. The authors of [4] have developed cost-effective water treatment systems that include devices such as a jet pump, a pulse power supply for the ozone generator, and a reactor for treating water with ozone, ensuring the purification of groundwater, surface, and wastewater to meet regulatory standards. The performance of ozonation devices depends on the degree of contamination and the volume of rinse solutions. The use of ozonation in combination with ultraviolet radiation and ultrasonic treatment increases the formation of hydroxyl radicals due to ozone transformation in the aqueous medium, yielding positive results [5].

The authors argue that the use of ozonation and ion flotation for water treatment is a promising method [6-8], despite the relatively high initial capital and operational costs associated with electricity consumption.

In the study of the wastewater treatment process of organic synthesis enterprises using the ozonation method, changes in the hydrocarbon composition are observed. The oxidation of hydrocarbons contained in wastewater by an ozone-air mixture results in the formation of final oxidation products—carbon dioxide and water—as well as the condensation of hydrocarbons.

The technology for processing technological solutions of copper production utilizing ozonation is shown here in [9] trial tests. Studies on the oxidation of pollutants in wastewater led to the determination of process parameters, including temperature, pH, ozone consumption, and time. These factors allowed wastewater to be purified and returned to production while also receiving a sludge of metal compounds. A method for ozonating wastewater from copper manufacturing has been devised based on the results. It was advised that JSC "Almalyk MMC" adopt the created technology. High ozone consumption, the need to organize and maintain reagent facilities and the high cost of the process are the disadvantages of ozonation.

One of the biggest industrial mining companies in Uzbekistan and Central Asia is JSC "Almalyk MMC." Extraction and concentration of sulfide, gold-bearing, and polymetallic ores, followed by the production of refined copper, metallic zinc, precious and rare metals, products based on them, and by-products, constitute the primary business activities of JSC "Almalyk MMC" [10]. JSC "Almalyk MMC" is conscious of the necessity of advancing and putting into practice contemporary methods and techniques for protecting the environment as well as for effectively using and conserving fuel and energy resources [11].

In some cases, chlorine and lime are used for neutralization. The main disadvantage of the chlorination method is the formation of organochlorine compounds, which are highly toxic, mutagenic and carcinogenic, and have the ability to accumulate in organisms, causing physiological changes and death. Lime forms gypsum sediments, which require separate storage in a tailing's storage facility.

Thus, ozonation is a promising method for processing process solutions and wastewater containing metals [12-16].

Researchers [17] studied the process of cleaning copper mine wastewater with pH 7 by deep ozone oxidation and claim that operating costs are slightly higher. With sulfuric acid solutions, the ozonation process is more complex.

In the above study, a lot of work was done on the application of the ozonation process of process solutions, and corresponding solutions were proposed. During copper production, more than 10 types of process solutions are formed. The neutralization of each solution requires a separate approach.

2. Materials and Methods

The research object included ordinary water with a pH of 7.2 and process solutions from copper production: acidic effluents from the copper sulfate shop, rinse solutions from the sulfuric acid shop of the Almalyk Mining and Metallurgical Combine (AMMC), and solutions obtained from the sulfuric acid leaching of oxidized copper ores. The volumes of the process solutions were as follows: acidic effluents – 50 m^3/day; rinse solutions – 2400–2800 m^3/day; sulfuric acid solutions – 20–25 m^3/day.

Table 1: Results of chemical analysis of technological solutions of copper production

Analyzed product	Chemical composition, g/dm3								
	H_2SO_4	Cu	Zn	Fe	Ni	Mo	Pb	S	Al
Acidic wastewater from the copper sulphate shop of the MPZ	4	0,035	0,001	0,02	12,5	0,002	-	0,001	0,0001
Washing solution from the SCC MPZ	48	0,026	0,012	0,019	0,002	0,0012	0,0001	0,03	0,0003
Solutions obtained during sulfuric acid leaching of oxidized copper ores	5	16,9	0,01	0,0041	-	0,00027	0,0001	0,023	0,0002

The results of the chemical analysis (table 1) indicate that the metals of industrial interest for extraction include copper, zinc, iron, nickel, and molybdenum. The complexity of processing the rinse solution is associated with its high acid content. In a glass reactor, the ozonation tests were conducted. A glass filter with a porosity of 40 mesh was positioned at the reactor's bottom to provide the gas, and the process solution being treated had a capacity of 1000 ml. Pure ozone was not used in the studies; instead, an ozone-air mixture (ozone concentration 2.5 mg/L) produced by the ozone generator was used. The temperature range for the trials was 20-25°C. A pH meter was used to measure the liquids' pH variations [11].

It is important to note that each metal present in the process solution has a specific pH value at which its precipitation (removal) is most effective. This creates certain challenges for the ozonation process, requiring strict control over the pH value and ozone dosage. If the established operating conditions are violated, there is a risk of accumulating ions of released metals in the solution, which can be toxic.

Thus, based on the described reactions, the ozonation process can be used to extract salts of several heavy metals: sulfates, metal carbonates, and others from process solutions.

The study on the purification of process solutions and wastewater was carried out according to the methodology [8].

3. Results and Discussion

During the ozonation process, samples were taken every 10 minutes over the course of 1 hour and analyzed for metal content. In all experiments, the ozonation process was accompanied by the formation of a precipitate. The results obtained indicate the formation of a fine-dispersed precipitate, composed of metals and non-metals.

When studying the changes in pH of the research objects during ozonation, it was found that within 40 minutes, the pH for all objects dropped to values between 1.5 and 1.8 (Figure 1). The rate of ozone decomposition was maximal in all cases, which was caused by the impurities present in the solutions. The discrepancies in the pH values depend on the duration of ozonation. The differences in pH values depend on the duration of ozonation. In all cases, an increase in the duration of the process leads to the precipitation of impurities and a decrease in the pH of the solution. After 35-40 minutes of duration, due to the cessation of the interaction of ozone with impurities in the solution, the pH of the process in all cases will be almost the same.

The interaction of ozone with technological solutions depends on the content of impurities (contaminants) and the presence of ions of heavy non-ferrous metals. The ozone consumption per 1 mg of metal ions depends on the concentration of metals in the technological solutions and the contact time with ozone.

The change in the residual concentration of impurities in the technological solution occurs up to a certain level, including down to 0, after which the change stops. The time at which changes cease and the residual concentration of impurities in the technological solution are key technological characteristics of ozonation and depend on the concentration of ozone in the water and the initial concentration of impurities in the technological solution.

Thus, the process of oxidizing impurities in the technological solution with ozone is multistage. The oxidation reaction can be considered complete at the moment a precipitate (an amorphous, flocculent mass) of partially oxidized impurities appears in the technological solution, which can be separated by filtration. The oxidation products contain compounds with a higher molecular weight (the precipitate) that were not observed in the original technological solution. This is explained by the fact that, during ozonation, in addition to oxidation, condensation processes of non-metallic compounds also occur, as well as the formation of intermediate radical particles arising from radical processes that interact with each other, as well as due to the dehydration of ozonolysis products.

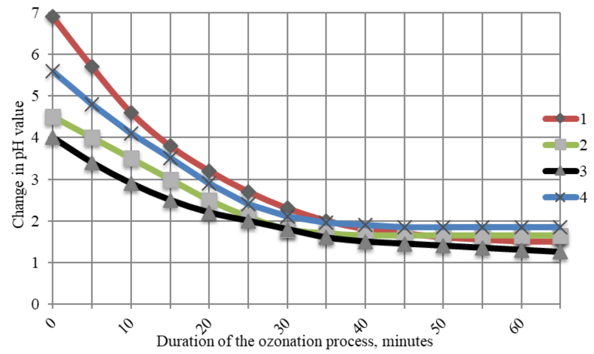

Figure 1: Dependence of pH value changes in different types of water on the duration of the ozonation process: 1- regular water, 2- acidic effluents from metallurgical production, 3- wash solutions from metallurgical production, 4- solutions obtained from sulfuric acid leaching of oxidized copper ores.

Chemical analyses showed that during ozonation, the studied solution accumulates oxygen-containing functional groups (OH^-, C=O, S=O). Data on the effectiveness of treating technological solutions with ozone are presented in Table 2. As a result of ozonolysis, the ratio of total compounds in the component composition of technological solutions changes. The content of metals, which make up the bulk of the metal-containing components, decreases by up to 99% during ozonation. The simultaneous precipitation of two or more different metal ions at a specific pH achieves better results than the precipitation of each metal separately.

This is explained by the process of forming mixed precipitates and the absorption of metal ions on the surface of the solid phase. Thus, there is a need to control the quality of the solution after ozonation based on several chemical and sanitary-hygienic indicators. Therefore, ozonation can be used as an effective method for neutralizing technological solutions from metallurgical production.

The recommended technological scheme for the ozonation treatment of technological solutions in copper production.

Based on the obtained experimental data, a conceptual scheme for the treatment of technological solutions in copper production through ozonation is proposed (Figure 2).

After the ozonation process, the silt is subjected to chemical examination. Depending on its composition, it is then delivered to the JSC "Almalyk MMC" zinc or copper smelting plant for traditional metal extraction techniques. For technological purposes, the pure solution is employed.

Table 2. Component composition of the initial and treated technological solutions

Composition of initial technological solutions			Composition of solutions after ozonation treatment		
Compounds	Concentration of substances, mg/l	Content of the total amount of determined substances, %	Compounds	Concentration of substances, mg/l	Content of the total amount of determined substances, %
Cu	19-35	2,50-2,81	Cu	0,1	1,84
Zn	1-49	0,13-3,93	Zn	0,03	0,55
Fe	41-200	5,39-16,05	Fe	0,001	0,02
Mo	0,27-2	0,04-0,16	Mo	0,01	0,18
Al	50-60	4,82-6,57	Al	0,3	5,51
Sulfates	650-900	72,23-85,38	Sulfates	5	91,89
Total content of substances		100	Total content of substances	5,441	100

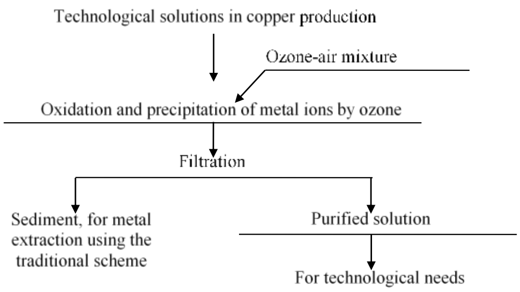

Figure 2: Technological scheme for the ozonation treatment of copper production technological solutions.

4. Conclusions

The study found that the pH of the solution, at which almost whole precipitation of metal ions takes place in the form of sediment, determines the level of purification of wastewater from copper manufacturing.

Under the influence of ozone, the chemical composition of the precipitated metals changes. Sulfate compounds of metals present in the technological solution decompose into metal ions and acid residues, and metal ions interact with hydroxide ions (OH^-), leading to the formation of metal precipitates.

Sulfates, metal carbonates, and other salts of various heavy metals can be eliminated from technical solutions by ozonation. An order of magnitude lower than the maximum allowable concentration (MPC) of metals in water, the concentrations of metals (Fe, Zn, and Cu) dropped to values <0.01 mg/l after an hour of treatment, minimizing environmental harm.

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