THE ISSUE OF METAL EXTRACTION DURING OZONATION PURIFICATION OF COPPER PRODUCTION PROCESS SOLUTIONS

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ABSTRACT

Over ten billion tons of minerals are mined worldwide each year, generating vast volumes of acidic process solutions rich in copper, zinc, iron, molybdenum and other metals. Effective treatment and resource recovery from these liquid wastes is essential both for environmental protection and for conserving strategic reserves. In this study, we investigate ozone-air bubbling as a single-stage purification and metal-extraction method for real copper-production effluents from JSC Almalyk MMC. Ozone consumption and metal liberation kinetics were quantified as functions of metal ion concentration, ozone dosage, and contact time. Under optimized conditions, more than 99 % of Cu, Zn, Fe and Mo was precipitated within one hour, driving residual concentrations below 0.01 mg L^{-1} and yielding a clear, reusable effluent. Based on these results, we propose a conceptual flow scheme that integrates ozone-induced oxidation of metal-ligand complexes with downstream hydroxide precipitation and filtration. This ozone-based process offers a scalable, chemical-free route to both recover valuable metals and produce high-quality process water, supporting closed-loop operation in copper refining and potentially other metallurgical industries.

Keywords: copper, ozonation, liquid wastes, purification, sulfuric acid, solution, oxidation, wastewater, ozone-air mixture.

INTRODUCTION

Industrial metal production generates significant volumes of waste streams that pose environmental risks if not properly managed. An emerging solution is the comprehensive valorization of these technogenic wastes via resource-recovery technologies [1]. However, recovering multiple metals from complex, multi-component process solutions remain a formidable challenge due to similar chemical behaviours among target species [2]. Integrating real-time monitoring, predictive modelling, and adaptive process control can mitigate these challenges and support sustainable regional development [3].

Researchers in Uzbekistan have demonstrated the potential of technogenic tailings as secondary resources. For example, Ingichka and Koytash tungsten-bearing wastes contain, on average, 769 g t^{-1} and 471 g t^{-1} tungsten, respectively, making them viable sources for recovery [4]. At Almalyk MMC, preliminary water-alkaline washing combined with calcination improved zinc oxide purity and enabled its reintegration into the hydrometallurgical cycle [5]. Similarly, a zero-waste treatment at the MEKHMASH plant, which combines Na_3PO_4/CaO dosing, skimming, filtration, and thermal evaporation, successfully reclaims valuable oil and produces clean effluent for reuse [6].

Using air in different processes bring different benefits. Using compressed air instead of argon for stirring the molten metal at the processing corrosion resistant stainless steels improves quality of steel and reduced chromium losses [7]. Thermodynamic calculations and found that $BaCaFeO_3$-δ is stable within a narrow range of oxygen partial pressures and temperatures, especially in oxidizing conditions [8]. Research also studied chlorine-air mixtures in pipelines [9]. Oxygen usage in high-organic-load blend of lead-zinc flotation and pyrite effluents also shows good results [10].

Ozonation has also been applied to diverse wastewaters. Researchers by knowing benefit of sorption processes found good solution for technologic problems [11, 12]. In nuclear power plant drain waters, combining ozone with natural bentonite and low-level iron/manganese reagents decomposes organic complexants and sorbs radionuclide analogues [13]. Electro-oxidation of artificial waters containing atrazine, bisphenol A, and chlorendic acid achieved rapid breakdown of bisphenol A to formic and oxalic acids and 96 % atrazine removal in three hours [14]. Electrical discharges and ultrasound further enhance ozone's degradation of surfactants and organics [15], and ultrasonic-ozone synergy has shown promise for accelerated copper leaching and recovery [16]. Ozone decomposition kinetics are strongly pH- and UV-dependent, influencing radical versus molecular pathways [17]. Advanced oxidation processes-combining ozone with hydrogen peroxide or ultraviolet light-convert residual organics in landfill leachate into low-molecular-weight species and markedly improve biodegradability and colour removal [18].

Applications extend beyond water treatment: manganese-based catalysts oxidize methane via ozone decomposition [19], and ozone disinfection removes tastes and odors from drinking water [20]. Ozone has proven effective for extracting non-ferrous and rare metals from wastes [21], enhancing gold recovery in cyanide leaching [22], and supporting silver dissolution [23]. It also achieves complex heavy-metal removal-reducing ammonia, copper, lead, zinc, and cadmium below stringent discharge limits in copper-mine effluents [24].

Optimizing these processes demands sound engineering design. Corona-discharge ozone generators must balance energy use, ozone yield, and capital cost to meet demand without excessive off-gas losses. High volumetric mass-transfer coefficients are achieved through careful scale-up using Sherwood-Reynolds-Schmidt correlations and preserving geometric and dynamic similarity. The "deep U-tube" reactor exemplifies this approach: its tall, narrow configuration sustains plug flow and high gas hold-up, outperforming conventional bubble columns in ozone efficiency [25]. Material selection (e.g., ozone-resistant alloys, fluoropolymers), off-gas destruction strategies, and lifecycle cost analyses complete the design toolkit for robust, economical ozonation systems.

EXPERIMENTAL

Material and methods

The objectives of this research are to study the possibility of using the ozonation process to extract metals from copper production process solutions. The object of the study was the process solutions of copper production of JSC Almalyk Mining and Metallurgical Plant (JSC Almalyk MMC): acidic wastewater from the copper sulfate shop of the Copper Smelter (g L^{-3}: H_2SO_4 - 4, Cu - 0.35, Zn - 0.001, Fe - 0.02, Ni - 12.5, Mo - 0.002), washing solutions from the sulfuric acid shop of the Copper Smelter (g L^{-3}: H_2SO_4 - 48, Cu - 0.026, Zn - 0.012, Fe - 0.019, Ni - 0.002, Mo - 0.0012), solutions obtained during sulfuric acid leaching of oxidized copper ores (g L^{-3}: H_2SO_4 - 5, Cu - 16.9, Zn - 0.1, Fe - 0.041).

Methodology for Ozonation of Copper Production Process Solutions. The ozonation process for treating copper production process solutions involves a recommended scheme for introducing the ozone-air mixture, which is designed to remove impurities that react rapidly with ozone (Fig. 1). For experimental studies, a bubbling absorber was selected and fabricated for the processing of process solutions [5]. The research was conducted using a setup with a low ozone production capacity. The accelerator's improved mixing causes ozone to be dispersed into tiny bubbles that range in size from hundreds of mm to 1 mm. This increases the surface area available for interaction and speeds up the pace at which O_3 dissolves in water.

Ozone formation is a multi-stage process that involves about 50 processes linked to ozone formation and breakdown, without which ozone generation is impossible [24 - 27].

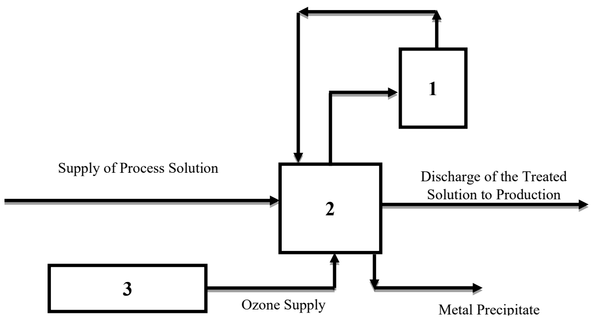

Fig. 1. Schematic of the ozonation process installation for copper production process solutions: 1 - waste gas collector; 2 - contact chamber; 3 - ozone generation unit.

Metal sulfate compounds present in the process solution in acidic environments decompose into metal ions and acidic residues. The metal ions interact with hydroxide ions (OH^-), resulting in the formation of metal precipitates:

$$MeSO_4 \rightarrow Me^{n+} + SO_4^{2-}, \quad (1)$$
$$Me^{n+} + OH^- \rightarrow Me(OH)_n\downarrow. \quad (2)$$

Calcium ions react with acidic residues:

$$CaCO_3 + SO_4^{2-} \rightarrow CaSO_4\downarrow + CO_3^{2-} \quad (3)$$

Copper sulfate interacts with carbonate ions and can form malachite:

$$2CuSO_4 + CO_3^{2-} + 2H_2O \rightarrow (CuOH)_2CO_3\downarrow + 2HSO_4^-. \quad (4)$$

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.

RESULTS AND DISCUSSION

During the ozonation of water, odors are completely removed at impurity concentrations up to 15 mg L^{-1}. Impurities in the technological solution are present in the form of ions and small particles, while ozone is mixed with air. The interaction between ozone and the technological solution goes through various stages, and the purification process by ozonation is multi-step.

The diffusion of ozone depends on its concentration in the solution, the concentration of ions, and the impurity content in the technological solution. Continuous ozone input into the treated solution, ozone consumption for oxidation reactions, and ozone's natural breakdown all affect the concentration of ozone in the solution. These mechanisms cause the water's ozone content to fluctuate (Fig. 2).

Curves 1 and 2 represent examples where the ratio of technological solution concentration to ozone is such that some excess ozone remains in the treated water. Depending on the magnitude of this ratio, the excess ozone may be higher (curve 1) or lower (curve 2).

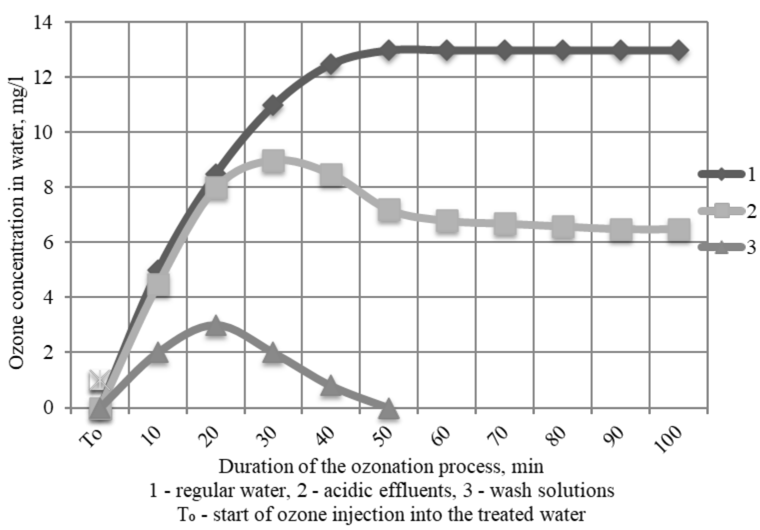

Fig. 2. Dependence of ozone concentration in water on the duration of the ozonation process.

When there are high concentrations of impurities in the technological solution, all the incoming ozone is used for oxidation and decomposition processes, and at a certain point, the ozone concentration in the water drops to zero (curve 3). With a constant volume of technological solutions and a constant ozone supply to the treatment unit, oxidation processes occur rapidly at first, resulting in high ozone concentrations and impurity levels. Then the oxidation rate slows down, and the concentration of impurities in the technological solution decreases.

The process of extraction (oxidation) of metals from the process solution with ozone is multi-stage. The appearance of sediment indicates the beginning of the interaction of impurities of the process solution with ozone. After a certain time, the solution is filtered, and the purified solution is subjected to chemical analysis to determine the residual content of metals.

During the study, Fig. 3 and Fig. 4 shows the relationships between the concentration of metal ions in the solution and the duration of treatment. An

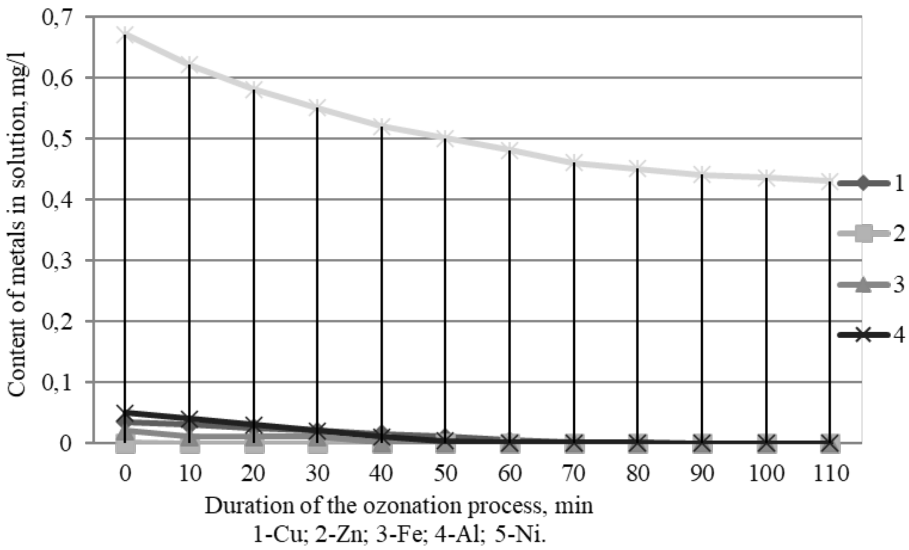

Fig. 3. Dependence of the change in metal content in the acidic effluents from the sulfate shop and content in washing solutions from the sulfuric acid leaching plant on the duration of ozonation.

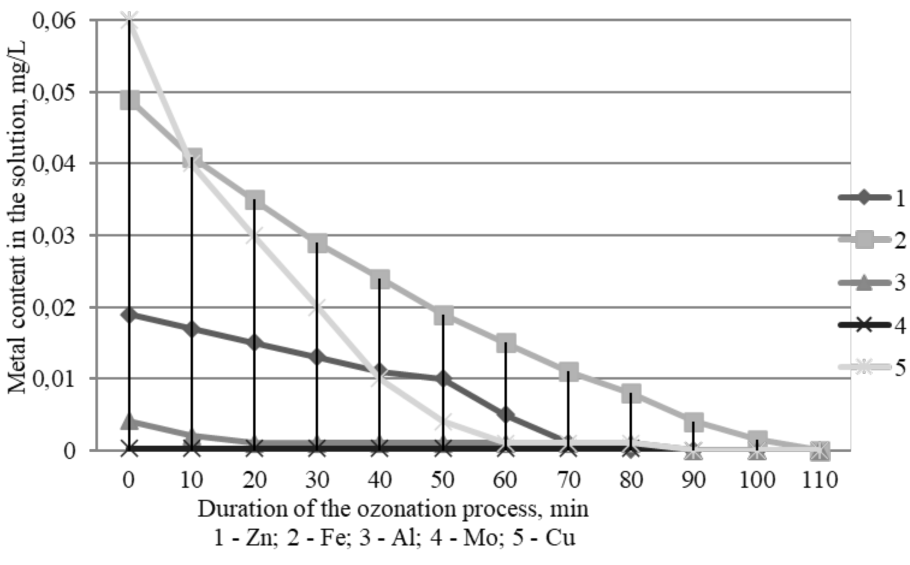

Fig. 4. Dependence of the change in metal solutions obtained during sulfuric acid leaching of oxidized copper ores.

Table 1. Changes in the metal content in the process solution before and after the ozonation process.

Composition of the solution	The metal content in the process solution, mg L^{-1}	Composition of solutions after ozonation treatment, mg L^{-1}
Cu	35	0.1
Zn	49	0.03
Fe	200	0.001
Mo	2	0.01
Al	60	0.3
Sulfates	900	5

order of magnitude lower than the maximum allowed concentration (MPC) of metals in water, the concentration of metals dropped to less than 0.01 mg L^{-1} after an hour of treatment. After more than an hour of treatment, the filtered solution was colourless and transparent (Table 1).

The core process in this scheme is the oxidation and precipitation of metal ions by ozone. The highly reactive ozone molecules oxidize metal ions present in the solution, converting them into higher oxidation states. For example, ferrous ions (Fe^{2+}) are oxidized to ferric ions (Fe^{3+}), and copper ions may be transformed into insoluble copper hydroxides or oxides. These transformations lead to the precipitation of metal hydroxides or oxides, which can be readily separated from the liquid phase.

Following the ozonation process, the solution undergoes filtration, a critical step where the insoluble metal hydroxides and oxides formed during oxidation are physically separated from the purified solution. The solid precipitates, referred to as sediment, contain valuable metal compounds, which can be further processed through traditional metallurgical methods, such as pyrometallurgical smelting or hydrometallurgical leaching, to recover metals like copper, zinc, and others. This ensures that economically valuable metals are not lost in the waste stream and can be reintroduced into the production cycle.

The purified solution, now free from unwanted metal ions, is directed for technological needs within the production system. This purified liquid can be reused in various processes, such as cooling, washing, or as a feedstock in other chemical operations, thus promoting resource efficiency and minimizing the consumption of fresh water or raw materials. By recycling the purified solution, the overall sustainability and cost-effectiveness of the copper production process are significantly enhanced.

Scientifically, this technology provides a dual benefit: it facilitates the recovery of valuable metals from industrial effluents while simultaneously purifying the process solutions for reuse, thereby contributing to a more sustainable, closed-loop production system. The use of ozone as an oxidant is particularly advantageous due to its strong oxidative potential and environmentally benign by-products, primarily oxygen, making it a greener alternative compared to traditional chemical oxidants like chlorine or hydrogen peroxide. Moreover, the ozonation process is highly selective, allowing for the targeted removal of specific metal ions while minimizing the generation of hazardous waste.

CONCLUSIONS

One of the "environmentally friendly" technologies for extracting metals from process solutions is ozonation, where oxidation of chemical compounds occurs with the participation of hydroxyl radicals formed because of ozone's chemical transformations.

The use of ozonation increases the efficiency of metal removal from copper production process solutions.

It integrates oxidation, precipitation, and filtration processes to recover valuable metals and generate purified solutions, optimizing both resource use and environmental outcomes.

Research on the use of ozone for processing copper production process solutions has yielded positive results and created the basis for industrial implementation. The proposed technology ensures the extraction of valuable metals from industrial wastewater and simultaneously purifies process solutions for reuse, thereby contributing to the creation of a more sustainable closed-loop production system.

Authors' contributions

The initiators of the proposed article were S.K., R.M., A.K., R.S. and contributed significantly to the experimental section and the final manuscript. D.K. is responsible for checking the article, assessing the correctness of each process and introducing the basics. All authors considered the final manuscript in every possible way and made valuable additions. The authors contributed significantly to the article and confirmed the presented version.

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