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The Ozone Usage During Extraction of Metals from Sewage of Copper Production

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ABSTRACT: Nowadays the design capacity of a mining complex joint-stock society Almalyk Mining and Smelting Plant (JSC Almalykskу MMC) which is one of the largest enterprises in Uzbekistan is on extraction of cupriferous ore 31 million tone and zinc-lead ore of 0,5 million tone in a year. The copper-smelting plant is the finishing link in a copper chain of JSC Almalyksky MMC.

KEY WORDS:solution, copper, extraction, metals, sewage, copper production, concentrate, reagent, sulfuric acid, metal recovery.

I. INTRODUCTION

While metals production, solid waste and sewage are formed that pollutes ecology and leads to a loss of a valuable components. Usually sewage was moved to settlers from where after cleaning merged in natural reservoirs. Now processing by limestone and lime for sedimentation of fluorine and other connections in order that the dumped waters met requirements of pollution`s control is extended. In settlers the maintenance of such components as Cu, F, Ca, P, Mo, Fe, Zn and others significantly decreases, however the dumped sewage contains still defined the number of these connections. The dumped waters not only bring chemical compounds in natural reservoirs, but also lead to reduction of size them pH. As a rule sewage is sour and have pH = 1÷3.

The sewage containing connections, copper of zinc, iron and other metals it appears due to the production of various metals. For increase in profitability of production and the solution of environmental problems it is offered various methods of extraction of metals from sewage: electrolysis, extraction, neutralization, sorption, ionic flotation, etc. [2-5]. The short review of methods of sewage treatment from organic substances and ions of heavy non-ferrous metals are submitted in [2, 3] work. For purification of copper`s solutions and cadmium is offered hydrolysis, at the same time a part of copper remains in solution. Full purification of solution of copper and cadmium is carried out zinc dust. Process of cleaning is based on the difference of normal potentials of metals [3]. In the monograph [4] physical and chemical bases of sewage treatment are stated by flotation, classification of ways of floatation processing of sewage and rainfall is given. Technological schemes of purification of various sewage with use of flotation, the recommendation about their application, a design a flotation cells and data for calculation of floatation installations are provided, the experiment on floatation processing of sewage which is available in domestic and foreign practice is generalized.

In work [5] that at high concentration of copper it is expedient to carry out electrolysis. However, when concentration is significantly less, ions of copper are also effectively absorbed by coal and ion-exchange filters. Copper is removed in the course of a desalting. Besides, cleaning can be based on chemical processes in which the metal ion which is in solution enters chemical reaction as a result of which insoluble connection in water is formed.
Alkalifying (the slightly soluble substance $Cu\ (OH)_2$ is formed) sedimentation by Na_2S sodium sulfide is applied to formation of insoluble compounds of copper. Sedimentation of copper from water solution is conducted at pH=7,5-13,5 values. There is a possibility of transformation of salts of copper into carbonates. The copper carbonate (malachite) is insoluble in water and can be removed from solution. However, at extraction of metals from sewage higher a quantity of metals remains by the listed methods, in them and they can't be transferred to water resources.

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Now one of innovative technologies is the cleaning by means of ozone [6-9]. At purification of sewage with ozone, the possibility of their deep cleaning appears. In a consequence drains can be returned in water resources. Carry to ozonization as processes of oxidation of organic and inorganic compounds or neutralization by the ozone dissolved in water, and the oxidizing processes proceeding with the participation of the hydroxyl radicals which are formed as a result of chemical transformations of ozone. Ozone is one of the strongest natural oxidizers. Interaction of connections with ozone is characterized by multistage transformations with formation of the intermediate products having various reactionary ability in relation to the oxidizers participating in process. In practice it isn't possible to finish, as a rule, oxidation by a full mineralization of the organic compounds which are available in solution. From there is a need of quality control of water after ozonization on a number of chemical and sanitary and hygienic indicators.
The efficiency of removal of metals at ozonization depends on an ozone dose: the ozone dose, the less residual concentration of metals in the purified water is higher. In many cases even at small doses of ozone almost full removal of metals is reached. The ozone dissolved in water can form a number of active particles from which are the most important hydroxyl (IT) and ozone (O_3) radicals. In water solutions also formation of other active particles is possible (O_2, O, H_2O •, H_2O_2). However, despite formation of big set of various active particles with high oxidizing ability, these particles can't affect efficiency of water purification because of small time of life and low concentration.
The ozone consumption on destruction of pollutants sewage of substances depends on many factors: pH the water environment, concentration of harmful substances, concentration of ozone, a way of mixture, duration of contact of ozone-air mix with the conditioned sewage, etc. Ions of metals after ozonization are besieged in the form of insoluble hydroxides. Extraction of metals from waste solutions of copper production only of heavy metals, economically isn't expedient. On the other hand, this waste contains a significant amount of rare metals. And extraction of iron, rare metals in one product, i.e. a concentrate, could supply ferrous metallurgy with raw materials for receiving special grades of steel. For this reason waste solutions of copper production have to be exposed to complex processing with allocation from all of them valuable components.
The purpose of the real work is the research of a possibility of extraction of metals from waste solutions of copper production of JSC Almalyksky MMC the containing metals from which it is expedient to receive not only heavy non-ferrous metals, but also rare, precious, ferrous metals and nonmetallic raw materials.

For achievement of this purpose it is necessary to solve the following problems:
- studying of the chemical composition of waste solutions of copper production;
- a research of behavior of compounds of the metals which are in waste solutions of copper production when processing;
- to develop the technological scheme of extraction of metals from waste solutions of copper production.
Objects of a research are waste solutions of copper production of the Almalyk mining and smelting plant: uterine solutions of the shop of production of rare metals (SPRM) and sour drains of the vitriol shop of the Copper-smelting plant (MPZ).
Results of the chemical analysis are given in tab. 1.

Table 1.
Results of the chemical analysis of waste solutions copper and zinc productions

Product to be analyzed	**Sewage volume,m³*s 3,6*10³**	**Chemical composition, mg m-3**				
		H_2SO_4	**Cu**	**Zn**	**Fe**	**Mo**
Stock solutions	2÷5	25-28	2,289	0,228	0,206	3,71
Sour Waste	20-25	35-40	0,035	0,001	0,02	0,002

From Table. 1 it can be seen that copper, zinc, iron, and molybdenum are of industrial interest for metal recovery. The complexity of processing the wash solution is associated with a high acid content.
Collection of equipment for laboratory-enlarged tests. Ozonization of wastewater is an absorption process 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 speed of the process in the diffusion region, it is necessary to increase the contact surface of the phases. An increase in pressure is also effective for the absorption process.

The scheme for introducing an ozone-air mixture is recommended for the removal of impurities from sewage that react fairly quickly with ozone (Figure 1). This scheme is accompanied by the formation of gaseous products, requiring their

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separation from the air, in addition, ozone is not fully used in it.In order to increase the economic efficiency of the ozonization process, it is necessary to carry out the maximum absorption of ozone by means of sewage from its mixture with air over a short period of time. We chose and manufactured a bubble absorber for wastewater treatment. The basic technological scheme of the plant is shown in Fig. 2. Sewage enters the mixer 1 in which it mixes with the reagents to obtain the desired pH value, and then pumps 2 to the bubble absorber 3 and from there to the purified water reservoir 4. The ozone-air mixture enters the bubbler absorber with ozone ballon 5. The exhaust gases from the absorber are sent to the cleaning device 6 and then discharged to the atmosphere.

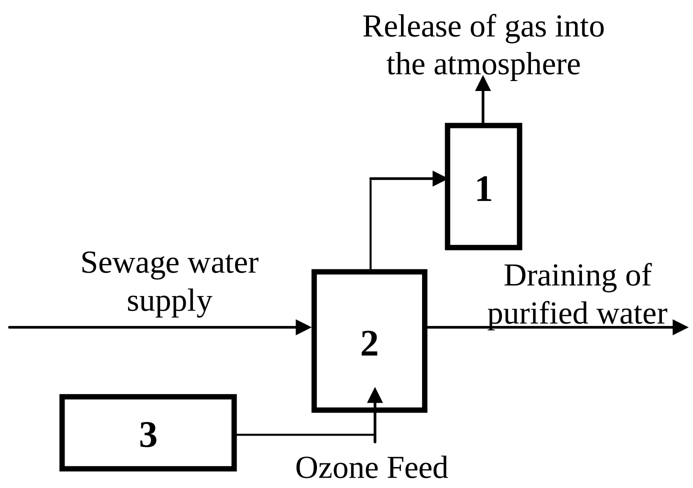

Fig. 1. Scheme of ozonation of water:
1 - Waste gas neutralizer; 2 - the contact chamber; 3 - ozone production unit

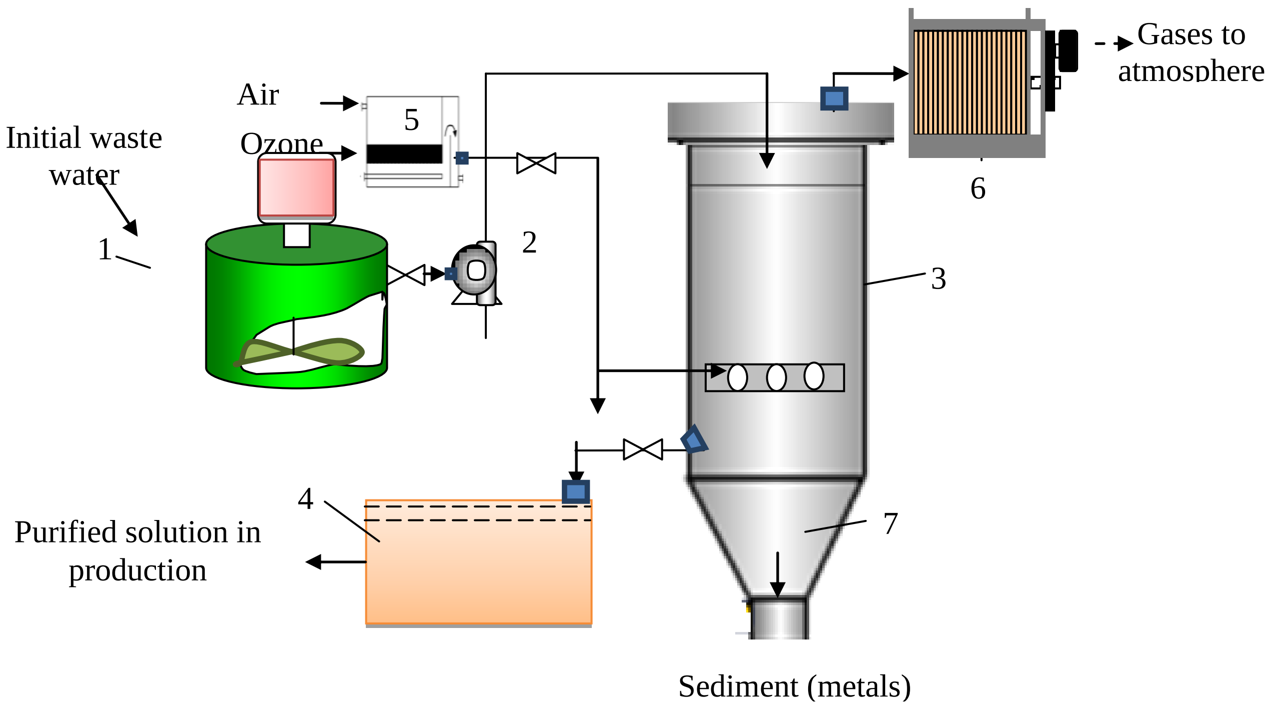

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Fig. 2. The basic technological scheme of the wastewater treatment plant by ozonation: 1 - mixer; 2 - the pump; 3 - bubble absorber (contact chamber); 4 - collection of purified solutions; 5 - ozone-air chamber; 6 - apparatus for cleaning off-gases; 7- special chamber for collecting solid particles.

As ozone approaches strong poisonous substances (surpasses, for example, hydrocyanic acid), in sewage treatment plants ozonization provides for the stage of purification of waste gases from ozone depletion. To this end, gases are diluted to safe ozone concentrations before they are released into the atmosphere, ozone destruction or its utilization. For the destruction of residual ozone, adsorption, catalysis or pyrolysis is used. During adsorption gases are passed through a column with active carbon in the form of grains with a diameter of 1-6 mm.
A bubble column 0.5 m high was used as a reactor. It was equipped with a fine-pore filter with a pore diameter of 70 ... 100 mkm for dispersing the ozone-air mixture, as well as fittings for exhaust gas removal and periodic sampling of treated water. The reactor operated in a flow-through mode over the gas phase and non-flowing over the liquid phase.
In the course of the study, the dependence of the concentration of metal ions in solution on the treatment time was studied. The results of the experiments are shown in Fig. 3 and 4.

From Fig. 3 and 4 it can be seen that for 8 hours of treatment the metal concentrations have decreased to a level <0.1 mg / l, which is an order of magnitude lower than the maximum permissible concentration of metals in water. The pH of the solution increased from 6.5 to 7.5. The filtered liquid with a treatment time of more than 7 hours was clear and colorless. During the experiments, the ozone-air mixture was fed into the reactor at a flow rate of 0.25 l / min and an ozone concentration of C = 6.0 mg / l. The initial pH values were within 4-5. The obtained data on the change in the concentration of metal ions as a function of the pH of the solution are shown in Table. 2.

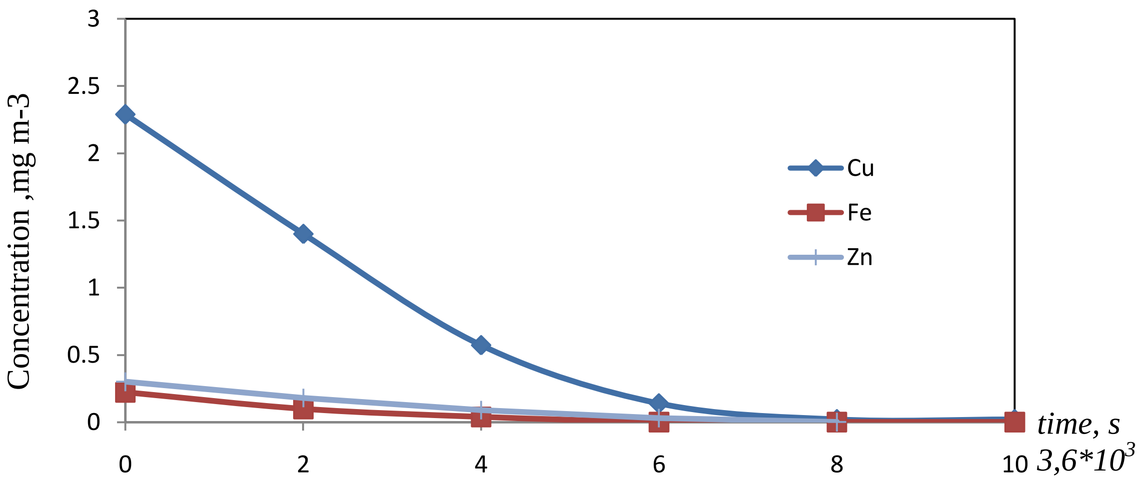

Fig. 3. Dependence of the concentration of metals in the mother liquors of the vitriolic shop on the processing time.

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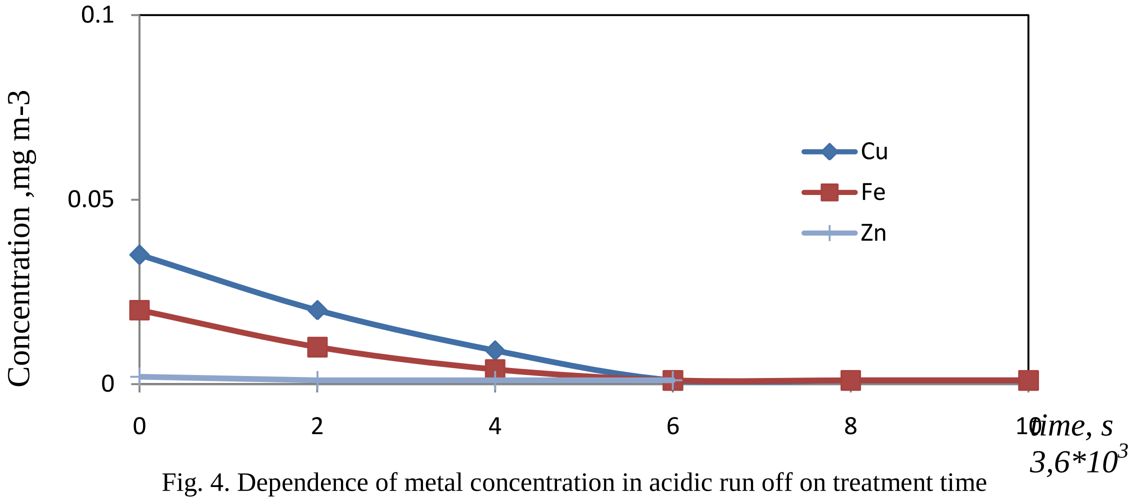

Fig. 4. Dependence of metal concentration in acidic run off on treatment time

Table 2.

Results of large-scale laboratory tests

The content in the mother liquor of MDCM MPZ, mg/l		pH solution	The content in solution after ozone purification, mg m-3				Sedimentation, mg m-3	Degree of sewage treatment, %			
			Cu	Zn	Fe^{+2}	Fe^{+3}		Cu	Zn	Fe^{+2}	Fe^{+3}
Cu	2289	6	92	57	103	0,5	7,6	96	75	34	99
Zn	228	7	22	14	56	-	9,4	99	94	64	100
Fe^{+2}	156	8	-	2,2	12	-	9,8	100	99	92	100
Fe^{+3}	53	9	-		1,5	-	10,1	100	100	99	100

The results of the experiments show that the maximum extraction of metals in the sediment is observed at pH = 8-9. The degree of purification of metals is 98-100%.

The efficiency of the process depends to a large extent on the pH of the solution being treated. Throughout the considered range of pH values of the solution, metal precipitation occurs in the form of solid particles. The maximum degree of extraction of Cu and Zn in the precipitate is observed at 8 and 9, respectively. The most complete precipitation occurs in nearby media, corresponding to the presence of metals in the form of hydroxides. To extract solids from the solution, the lower part of the bubble absorber is mounted a special chamber [10].

Recommended technological scheme. On the basis of the experimental data obtained above, a schematic diagram of the purification of waste solutions of copper production from metal ions by ozone is proposed (Fig. 5).

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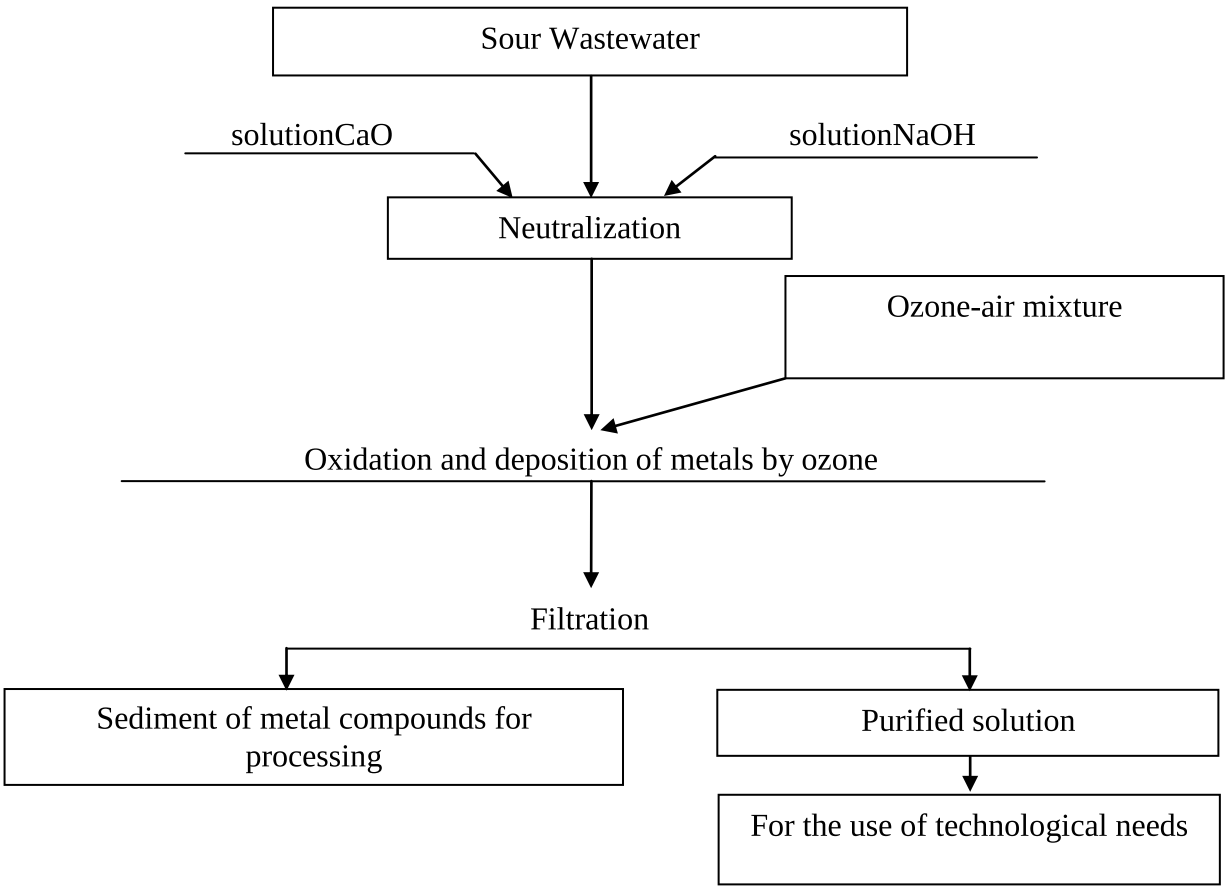

Fig. 5. The recommended technological scheme for sewage treatment of copper production

Acid waste solutions are neutralized with solutions of CaO and NaOH, an ozone-air mixture is added and subjected to ozonation. The high oxidation-reduction potential of ozone causes its activity to different by nature impurities of sewage. When ozone is dispersed, there are two basic processes - oxidation and disinfection. At the same time, there is a significant enrichment of the water with oxygen. In the contact chamber, the water to be purified and the ozone-air mixture are supplied countercurrent, which increases the efficiency of their interaction. During the process, the pollutants react with ozone. Sediment, metal compounds are subjected to further processing. After filtration, the purified solution is sent to use technological needs.

II. CONCLUSION AND FUTURE WORK

1. As a result of the studies carried out, the dependence of the degree of purification of waste solutions of copper production on the pH value of the solution determined that the optimum pH at which the almost complete precipitation of metal ions in the form of a sediment is achieved at pH 8-9.
2. Dependences of the concentration of metal ions in solutions on the treatment time were studied. It was found that for 8 hours of treatment the concentration of metals (Fe, Zn, Cu) decreased to <0.1 mg / l, which is an order of magnitude lower than the maximum permissible concentration of metals in water. The pH of the solution increased from 5.5 to 7.5.
3. The technological solutions found can be applied in other industries related to the processing of metal-containing products.

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