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The Results of Experimental Studies of Wastewater Disinfection of Metallurgical Production with Ozone

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ABSTRACT: The paper presents the results of experimental studies of wastewater disinfection of metallurgical production with ozone. All possible reactions of ozone formation, reactions with metal ions, and precipitation reactions are presented. Based on the reaction described, the ozonation process can be used to remove a number of heavy metals from the wastewater salts: sulfates, metal carbonates, etc.

KEY WORDS:process, reaction, ozone, ecology, ion removal, neutralization, solution..

I.INTRODUCTION

The choice of the method for the wastewater disinfection of metallurgical production is carried out on the basis of the flow rate and quality of treated wastewater, the conditions for the supply and storage of reagents. Furthermore, the choice of disinfection method is determined not only by technical and economic indicators, but also by environmental requirements. Ozone is one of the strongest oxidizing agents; it oxidizes all metals except gold and platinum metals, as well as most non-metals. It converts lower oxides to higher ones, and metal sulfides to sulfates. Therefore, the use of ozone for wastewater treatment has a dual purpose: to ensure disinfection and improve the quality of treated water.

The reactions of ozone with components found in wastewater have been little studied, therefore, a preliminary step in the development of wastewater ozonation technology is conduction of preliminary technological studies.

The development and use of ozone technologies are based on the high reactivity of ozone and its ability to decompose quickly, without forming by-products polluting the environment. The only drawback is the relatively high cost of ozone. However, with the development of new energy-saving constructions of ozonizers and stricter environmental requirements in relation to traditionally used chemicals, ozonation methods arebecoming competitive.

II. SIGNIFICANCE OF THE SYSTEM

Due to its significant oxidizing ability, ozone exerts effekt to a greater or lesser extent on all metals with a relatively high value of the redox potential. It should be noted that for each of the metals present in the treated water, a certain pH value is characteristic at which they are most completely removed. This circumstance creates certain difficulties in ozonation, requiring strict control over the pH value and dose of ozone, since in the event of violation of the established operating conditions, ions of released metals accumulate in water, which can be toxic.

III. METHODOLOGY

During the development of each individual spark, electrochemical reactions occur, the result of which is the formation of ozone and its decomposition. The ozone formation process consists of several stages, and more than 50 reactions associated with the formation of ozone and its decomposition, without which it is impossible to obtain ozone. In

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ozonizers, an ozone-air mixture is produced under the action of an electric discharge on oxygen in the air, and oxygen molecules and the synthesis of ozone molecules decompose under the influence of external energy:

O_2 + энергия ↔ O + O, (1)

O_2 + O ↔ O_3 + энергия, (2)

the time constant of these processes is very small and amounts to a few nanoseconds.

The next step is the formation of an ozone molecule:

$O + O_2 + M \rightarrow O_3 + M$, (3)

in which the third particle M takes part: a molecule, ion, electron or atom in a neutral or excited state.The formation of ozone requires a time of up to 10 μs, in addition, during the movement of gas particles, O_3 molecules decompose according to the reaction:

$O_3 + M \rightarrow O_2 + O + M$. (4)

The higher the temperature, the more intense this reaction.

As a result of the passage of the working gas through the discharge zone of the ozonizer, an ozone-air or ozone-oxygen mixture with an ozone concentration (0,1-10 g/m^3) is obtained at the outlet.In dry air, ozone slowly decomposes to form oxygen:$O_3 \leftrightarrow O_2 + O$ (5)

$O + O_3 \leftrightarrow 2O_2$ (6)

$2O_3 \leftrightarrow 3O_2$ (7)

The process is accelerated in the presence of catalysts and with increasing air humidity.Therefore, in moist air, ozone exhibits a strong corrosive effect.In water, ozone decomposes according to a radical mechanism and is accompanied by the formation of peroxide compounds and free radicals OH^-, HO_2^-:

$O_3 + H_2O \rightarrow 2OH\bullet + O_2$, (8)

$O_3 + OH^- \rightarrow HO_2\bullet + O_2^-\bullet$, (9)

$O_3 + HO\bullet \rightarrow O_2 + HO_2\bullet \leftrightarrow O_2^-\bullet + H^+$, (10)

$O_3 + HO_2\bullet \rightarrow HO\bullet + 2O_2$, (11)

$2HO_2\bullet \rightarrow O_2 + H_2O_2$, (12)

$OH\bullet + HO_2\bullet \rightarrow O_2 + H_2O$, (13)

$OH\bullet + OH\bullet \rightarrow H_2O_2$, (14)

$O_3 + H_2O_2 \rightarrow OH\bullet + HO_2\bullet + O_2$. (15)

The mechanism of ozone decomposition for carrying out water purification from the Me substance by the ozonation method, the decay rate is: direct reaction of ozone with the substance (O_3 + Me → O_2 + Me-O, where Me is a metal-containing substance) and a decrease in ozone concentration under the influence of the generated particles in the chain reactionradical mechanism of ozone decay (O_3 + M → O_2 + M-O•), where M is hydroxide ion OH^-, hydroperoxide ion HO_2^-, superoxide ion-radical O_2•-, hydroxyl radical OH•.Substances in ozonated water are able to initiate, enhance the effect, or reduce the rate (inhibit) of radical chain reactions involving ozone.OH^-, H_2O_2/HO_2^-, Fe^{2+} are able to excite the formation of the superoxide ion O_2^-• from the ozone molecule. The regeneration of superoxide ions from hydroxyl radicals requires promoters (a substance added in small quantities in order to improve its properties, such as activity, selectivity or stability.) R_2-CH-OH, aryl radicals, O_3.Inhibitors can help establish a hydroxyl-radical bond without regeneration of a superoxide anion (an ion of an oxygen molecule with an unpaired electron).

Ozone resilience depends on the pH of the medium and on the composition of the treated wastewater. The effective use of ozone is depends on the stability of ozone in water and aqueous solutions. At low ozone concentrations, the accumulation of ozone decomposition products by a chain mechanism occurs. Calcium, magnesium and barium carbonates have an order of magnitude higher efficiency for the catalytic decomposition of ozone in water than sulfates of these metals. This may be due to the interaction of carbonate and bicarbonate anions with ozone and their inclusion in the chain of radical reactions.

The increase in the degree of wastewater treatment in the presence of iron (II) sulfate is explained by the fact that iron (II) cations present in the wastewater and iron (III) cations formed as a result of oxidation catalyze the radical chain oxidation process.During the interaction of the iron (II) cation with oxygen and hydrocarbon (RH), the nucleation of the chain in the initial stage occurs as follows:

$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^-\bullet$, (16)

$H_2O + O_2^-\bullet \rightarrow HO^- + HO_2\bullet$, (17)

$2HO_2\bullet \rightarrow H_2O_2 + O_2$, (18)

$H_2O_2 + O_2^-\bullet \rightarrow HO^- + O_2 + HO\bullet$, (19)

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO\bullet$, (20)

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$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + 2HO^-$, (21)
$H_2O_2 + HO\bullet \rightarrow H_2O + HO_2\bullet$, (22)
$Fe^{2+} + HO_2\bullet \rightarrow Fe^{3+} + HO_2^-$, (23)
$Fe^{3+} + HO_2^- \rightarrow Fe^{2+} + H^+ + O_2^-\bullet$, (24)
$Fe^{3+} + HO_2^- \rightarrow Fe^{2+} + HO_2\bullet$, (25)
$RH + Fe^{3+} + O_2^-\bullet \rightarrow (FeOH)^{2+} + RO\bullet$, (26)
$RH + Fe^{3+} + O_2^-\bullet \rightarrow (FeOOH)^{2+} + R\bullet$, (27)
$RH + Fe^{3+} \rightarrow Fe^{2+} + H^+ + R\bullet$, (28)
$R\bullet + O_2 \rightarrow RO_2\bullet$, etc. (29)
The following reactions occur during chain nucleation using ozone:
$Fe^{2+} + O_3 \rightarrow Fe^{3+} + O_3^-$, (30)
$Fe^{2+} + O_3 + H_2O \rightarrow Fe^{3+} + O_2 + 2OH^-$, (31)
$RH + O_3 \rightarrow RO_3H \rightarrow R\bullet + O_2 + HO\bullet \rightarrow RO_2\bullet + HO\bullet$, (32)
$RH + Fe^{3+} + O_2^-\bullet \rightarrow (FeOH)^{2+} + RO\bullet$, (33)
etc.
Ozonation of Fe (II) leads to the formation of OH radicals in a solution:
$Fe^{2+} + O_3 \rightarrow FeO + O_2$, (34)
$FeO^+ + H_2O \rightarrow Fe^{3+} + OH\bullet + OH^-$. (35)
Iron in the formation of OH^- radicals, reacts with metals and form metal hydroxide:
$Fe(OH)^{2+} + Me \rightarrow Fe^{3+} + MeOH$. (36)
Ozone in a sulfuric acid solution oxidizes metal compounds to compounds of higher valency:
$2FeSO_4 + H_2SO_4 + O_3 = Fe_2(SO_4)_3 + H_2O + O_2$. , (37)
The efficiency of iron removal during ozonation depends on the dose of ozone, the higher the dose of ozone, the lower the residual concentration of iron in purified water.Ozone dissolved in water forms a number of important active particles: hydroxyl (OH•) and ozonide ($O_3\bullet$) radicals.Other active particles (O_2, O, $HO_2\bullet$, H_2O_2) are formed in aqueous solutions.
Sulfate metal compounds found in wastewater under acidic conditions decompose into metal ions and acid residues, metal ions interact with hydroxide ion OH^- and metal precipitates are formed:
$MeSO_4 \rightarrow Me^{+n} + SO_4^{2-}$, (38)
$Me^{+n} + OH^- \rightarrow Me(OH)_n\downarrow$. (39)
In wastewater there are calcium ions, which react with acid residues:
$CaCO_3 + SO_4^{2-} \rightarrow CaSO_4\downarrow + CO_3^{2-}$ (40)
Copper sulfate interacts with the carbonate ion and malachite can form:
$CuSO_4 + CO_3^{2-} + 2H_2O \rightarrow (CuOH)_2CO_3\downarrow + H_2SO_4^{2-}$. (41)
Thus, on the basis of the described reaction, the ozonation process can be used to remove a number of heavy metals from the wastewater salts: sulfates, metal carbonates, etc.
The object of the study was the wastewater of copper and zinc production: acidic effluents of sulphate shop, washing solutions of the sulfuric acid shop of the Smelter and Zinc Plant.

IV. EXPERIMENTAL RESULTS

The maximum of wastewater treatment in an acidic medium can be explained by a chemical process accompanied by an enlargement of ion molecules (reactions of hydroxyl and peroxide radicals with a high value of oxidizing potential) and the formation of a precipitate, which is confirmed by the amount of solid fine phase formed.
For ten to twenty minutes, occurs the interaction of ozone with easily oxidized substances in wastewater.However, as can be seen from Fig. 1, the impurity content noticeably decreases after an hourly treatment, and then stabilizes.It can be assumed that in the process of ozonation there is not only surface oxidation of metals, but the formation of peroxides, which, by diffusion penetrates deep into the particles, cause secondary oxidation processes.
It was shown that in the process of wastewater ozonation, an increase in the content of active oxygen occurs.During the study, the dependence of the concentration of metal ions in solution on the treatment time was studied.From fig.2 and 2, and table.1 it can be seen that after 1 hours of treatment, the concentration of metals decreased to a level of <0,1 mg/l, which is an order of magnitude lower than the MPC of metals in water.Filtered liquid with a treatment time of more than 1 hour was transparent and colorless.

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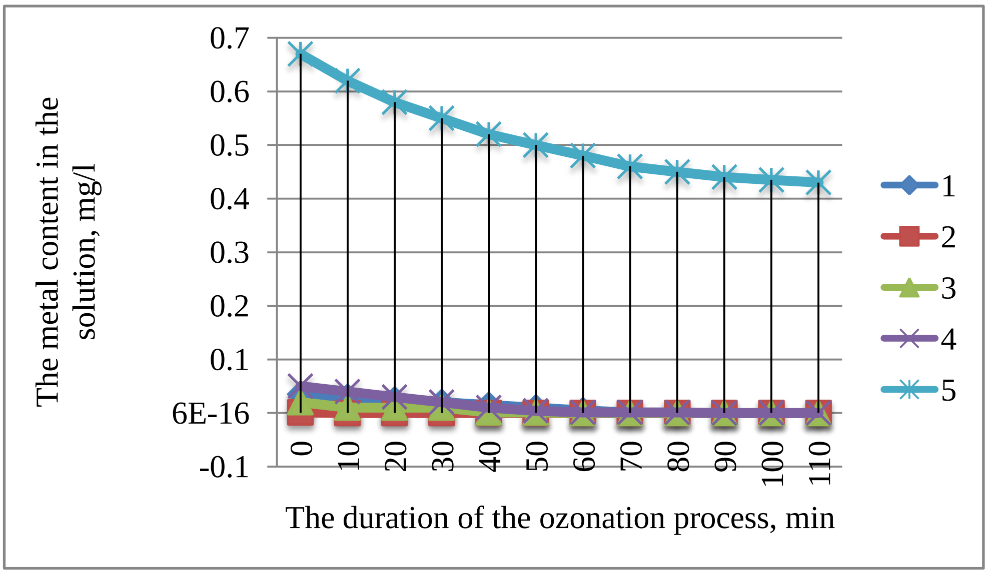

Fig. 1 Effect of ozonation time on the content of impurities of acidic effluents of vitriol shop:

1-Cu; 2-Zn; 3-Fe; 4-Al; 5-SO_4.

The amount of co-precipitation of two or more different metal ions, at a certain pH, achieves better results than the precipitation of each metal separately. This is explained by the formation of mixed precipitates in the sediment and the absorption of metal ions on the surface of the solid phase.

The results of enlarged laboratory tests of the treatment of waste solutions (waste water) of copper and zinc production show that the maximum extraction of metals into the precipitate is observed at the beginning of the process. The degree of purification of metals is 98-99%.

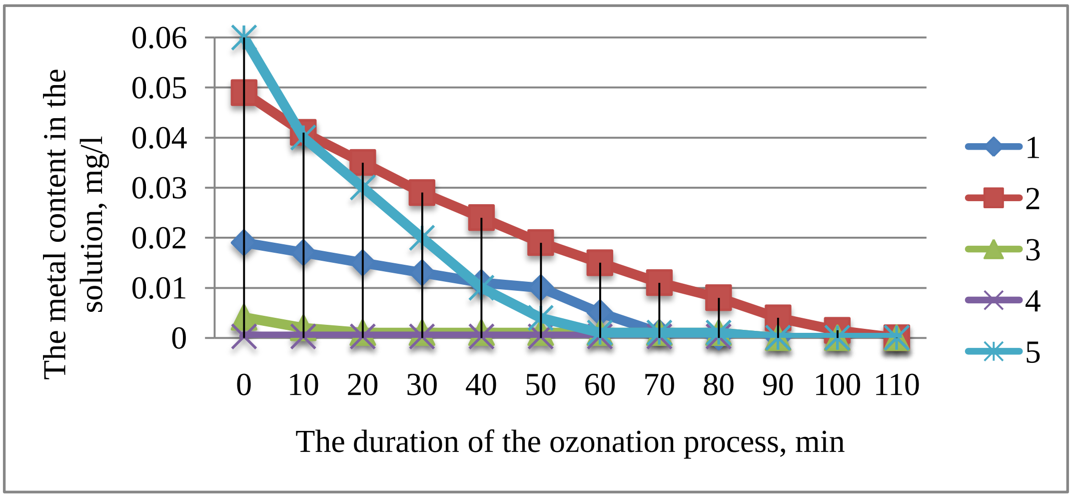

Fig.2 Effect of ozonation time on the content of impurities in washing solutions of copper s me Hing plant and zinc factory:1-Cu; 2-Zn; 3-Fe; 4-SO_4; 5-Al.

Table 1 The composition of the source and treated wastewater

The composition of the source wastewater after ozone treatment			The composition of the source wastewater after ozone treatment		
Compounds	Concentration of substances, mg/l	Content from the total amount of certain substances, %	Compounds	Concentration of substances, mg/l	Content from the total amount of certain 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
Sulphates	650-900	72,23-85,38	Sulphates	5	91,89
Total content		100	Total content	5,441	100

Wastewater after ozonation, in terms of quality meets the requirements of the MPC, by achieving a high degree of water purification from metal cations of copper, zinc, iron, nickel, lead, cadmium, etc.

V. CONCLUSION AND FUTURE WORK

Thus, as a result of the conducted studies, the degree of purification of the waste solutions of copper and zinc by ozonation was determined to depend on the pH of the solution, at which almost complete precipitation of metal ions in the form of precipitates is achieved.Sulfate metal compounds found in waste water decompose into metal ions and acid residues, metal ions interact with hydroxide ion OH- and metal precipitation is formed.Ozonation can be used to remove a number of heavy metals, sulfates, salts metal carbonates, etc. from wastewater. It has been established that after 1 hours of treatment, the concentration of metals (Fe, Zn, Cu) decreased to a level of <0,1 mg / l, which isan order lower than the MPC of metals in water.Based on the studies, a basic scheme of wastewater treatment of copper and zinc production by ozone is proposed.

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