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COMPOSITIONAL CHARACTERISTICS OF SLUDGES GENERATED IN INDUSTRIAL ENTERPRISES AND THE THEORETICAL FOUNDATIONS OF THEIR PROCESSING TECHNOLOGIES

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Abstract: This paper discusses the theoretical foundations of integrated technologies for the processing and utilization of heavy compounds of non-ferrous metals contained in industrial waste, as well as opportunities for reducing environmental pollution.

Key words: heavy metal ions, sludge, maximum concentration, coagulation, acids, alkalis, crystallization.

1. Introduction

The issue of environmental pollution resulting from the intensive operation of industrial enterprises is one of the most pressing issues that requires public attention and the timely development of effective technological solutions [1]. Within the metallurgical industry, a significant number of enterprises employ the utilisation of coatings, derived from aqueous solutions or molten salts of metals, on metal components during the manufacturing process. This practice is undertaken with the objective of enhancing the corrosion resistance of the components and thereby ensuring an augmented level of durability when subjected to external environmental factors.

During production processes, it has been found that toxic wastewater containing heavy metal ions such as Cr^{6+}, Cd^{2+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Ni^{2+}, Pb, and others is generated [2]. In enterprises of the Republic of Uzbekistan, thousands of tons of heavy metal compounds are released into the environment annually. One of the factors exacerbating this situation is that many enterprises engaged in electroplating do not have fully operational local treatment facilities or fail to

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completely neutralize toxic components [3]. As a result, the wastewater sludges from such industrial enterprises are discharged in large quantities into waste disposal sites.

Another pressing issue is that, in the metallurgical industry, wastewater treatment processes produce large volumes of sludge. These sludges contain, on the one hand, substances that pose a risk to the natural environment and, on the other hand, valuable components that can be reused in various technological processes after regeneration or neutralization [4]. The recovery of sludges allows for the efficient utilization of these substances, conserving natural resources while significantly reducing the harmful impact of sludges on the environment. This is because the content of non-ferrous metals in the sludges from treatment facilities is close to that of natural raw materials, making the ecological and economic importance of industrial waste utilization substantial.

During the wastewater treatment process, the following objectives are achieved:

Precipitation of heavy metals in the form of hydroxides;

Separation of colloidal and suspended particles as sludge;

Complete reduction of hexavalent chromium to trivalent chromium.

Materials and Methods

The neutralization of concentrated acidic and alkaline media is carried out by their mutual reaction, whereby the pH of the wastewater being treated is adjusted to a range of 6.5–8. In cases where the acidic solution is in excess, an alkaline solution is added, and conversely, if the alkaline solution is in excess, the corresponding amount of acid is introduced. According to technological data, industrial wastewater from the electroplating section flows into the neutralization unit, where it is completely detoxified.

The incoming wastewater includes:

- Concentrated acid containing chromium;
- Concentrated alkaline solution.

The volume of wastewater entering the neutralization unit (30 m^3/day) consists of compounds of zinc, iron, chromium, and copper, as well as suspended particles to be detoxified.

During the treatment of acidic and alkaline wastewater, the pH of the aqueous medium is adjusted using acid or alkaline reagents to a level at which heavy metal cations precipitate as sparingly soluble hydroxides (see Table 1). In this way, wastewater is detoxified, and excess acid or alkali is converted into neutral salts. The target pH for neutralization is 8.5–10. Exceeding this pH is not recommended, as it increases the time required for complete wastewater neutralization.

Precipitation Limits of Metal Hydroxides

Table 1

№		**Precipitation medium pH**

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	Heavy metal ions	Onset of Precipitation	Complete Precipitation
1	Cr^{+6}	6,5	9,3
2	Cd^{+2}	4,5	7,2
3	Zn^{+2}	6,5	8
4	Cu^{+2}	4,5	7,1
5	Fe^{+3}	1,7	4,3
6	Fe^{+2}	5	7,5
7	Ni^{+2}	6,5	8,5
8	Pb,	5	6,5

The neutralization process is carried out in the following sequence

$$CuSO_4+2Na0H = Cu(OH)_2+Na_2SO_4$$

$$FeC1_3+3NaOH = Fe(OH)_3+3NaC1$$

$$Cr_2(SO4)_3+6Na0H = 2Cr(OH)_3+3Na_2SO_4$$

$$ZnO+2NaOH = Na_2ZnO_2+H_2O$$

$$NaOH+HC1=NaC1+H_2O$$

Results and Discussion

As a neutralizing agent for acidic wastewater, a 40–45% concentrated liquid alkaline sodium solution of grade RD–1 or technical sodium hydroxide compliant with GOST 2263–79 can be used. For the neutralization of alkaline wastewater, a 27–30% concentrated technical hydrochloric acid compliant with GOST 857–78 can be applied. The main drawback of the existing treatment method is the high water content in the sludge after purification. The water in the treatment sludge forms colloidal systems consisting of finely dispersed, insoluble particles and remains suspended in various liquids. Typically, sludges containing heavy metal hydroxides are highly toxic and contaminated with organic and mineral impurities. Each year, 3–4 tons of sludge with approximately 95% water content are generated. These sludges are temporarily stored in sludge storage facilities and later sent for detoxification after the addition of coagulants. Therefore, prior to any method of galvanic sludge utilization, it is necessary to remove the water from the sludge.

Methods for separating sludges from water include reagent-free technologies, such as electrocoagulation. The use of chemical agents for the sedimentation of finely dispersed sludges allows for a reduction in process duration, minimizes production space requirements, ensures continuous operation, and improves the quality of treated water. Water separation of sludge by freezing is also known; however, this technology requires a significant amount of electrical energy. The reuse of sludges or materials separated from them contributes to the conservation of natural resources and reduces the amount of waste discharged into the environment. Dewatered galvanic sludges are widely applied in the construction materials industry. To mitigate the ecological hazards of industrial waste, chemical fixation methods are employed to stabilize toxic compounds in the sludge. Fixation is carried out through ferritization, silicatization, reinforcement with binding materials, and the synthesis of a solid phase. Thus, chromium-containing sludges, after drying, are widely used in the production of decorative glass as well as in the manufacture of paint pigments. Depending on the composition of the sludge, glasses of various colors can be obtained, including green, blue, brown, black, and their shades. The powder obtained from drying the sludge, up to 10% by weight, can enhance the glossiness of ceramic decorative tiles. Incorporating 3% of sludge powder into construction ceramic mixtures improves their mechanical strength. The ceramic mixture is fired in a tunnel kiln at a temperature of 980°C. In brick production, 3–5% of water-extracted sludge (with a moisture content of 60–80%) is added to the clay, improving the technological properties of the mixture. Industrial hydroxide sludges are also used as binding materials in asphalt concrete. During road pavement operation, the minor dispersion of asphalt particles does not significantly affect the chemical composition of the soil or drainage water. Iron-containing sludges, after drying, are used to produce expanded clay (keramzit) and high-quality ferrites. Sludges are also applied in the manufacture of roofing materials (such as roof tiles or shingles). Incorporating heavy metal sludges into ceramic mixtures not only ensures their reliable detoxification but also improves the strength properties of roofing materials. One of the most promising directions for secondary utilization of sludges is their processing using hydrometallurgical methods, which allow the selective recovery of almost all non-ferrous metals. In such processes, the moisture content of the sludges should not exceed 10%, and individual pieces should not weigh more than 1 kg. It is important to consider that different metal sludges (e.g., zinc and nickel) are not always compatible. Therefore, in many cases, metal recovery from sludges is not performed, and the sludges are used as additives for the production of various materials. Thus, the sludges generated from technological baths and the residues formed during the neutralization of spent electrolytes typically represent a concentrated source of heavy metals. Currently, they are utilized to a limited extent in the following main directions:

As a coloring agent in glass production;

For obtaining mineral pigments for various purposes;

For the production of various targeted alloys through metallurgical processing.

For the secondary utilization of sludges, the use of a filter press is recommended as the optimal method for water separation. A batch-operated filter press easily separates mechanical mixtures of solids, whether crystalline or amorphous, and liquids from various suspensions under pressure. When a filter press is used in the technological process, the sludge is produced in an almost dry state and can be stored in specialized containers. The composition of the sludge is as follows: moisture — 47.5%, Zn — 5%, $Cr(OH)_3$ — 1%, as well as zinc, nickel, copper, iron, and other hydroxides. Since the sludge is produced almost dry and can be sent directly for processing without prior storage in sludge facilities, the elimination of sludge storage is possible. Given that galvanic sludge represents valuable secondary raw material, it is not advisable to send it directly for disposal. One promising approach is to transfer the sludge to specialized enterprises where it can be used as secondary raw material in the production of decorative glass. It is also applied in the production of glazes and coatings used in decorative glass and construction materials (e.g., glass-keramzit production). Additionally, in the production of construction and household ceramics, chromium-containing and other dewatered galvanic sludges resulting from reagent-free wastewater treatment are utilized. Glass firing is carried out in a 0.5-ton capacity rotary

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drum kiln. The glass mixture consists of sand, aluminum, boric acid, dolomite, soda, fluorite, and chromium-containing wastes. The firing temperature is 1340°C, corresponding to the proposed glass's upper crystallization limit of 810–870°C.

Conclusion

Thus, the use of a filter press allows for the elimination of sludge storage facilities, thereby reducing both the volume of generated waste and the disposal fees associated with waste classification and hazard level. In addition, this approach enables more efficient use of natural resources and minimizes the environmental impact of metal production.

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