CONSTRUCTION OF THE ALGORITHM FOR ASSESSING THE ENVIRONMENTAL SAFETY OF GALVANIC SLUDGES

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1. Introduction

One of the most pressing environmental issues for industrial enterprises, which employ galvanic processes in their technological cycle, is the problem of accumulation of generated waste, so-called galvanic sludge (GS) [1, 2]. GS containing heavy metals (HM) is a source of biotic, mechanical, chemical, and other types of pollution [3, 4].

At present, there are no uniform theoretical and methodological frameworks for ensuring environmental safety
within the system of galvanic industrial waste management. Unambiguous approaches and algorithms have not yet been developed to assess its ecotoxicological hazard.

A scientific solution to this issue may be the development of unified scientific and methodical approaches to a comprehensive assessment of the level of environmental safety of GS, with a direct study into their anthropogenic impact on natural objects.

2. Literature review and problem statement

Paper [5] reports a procedure of comprehensive assessment of identification and systematization of existing sources of environmental hazard. The main study elements have been identified: identification of sources of environmental hazards, assessment of the degree of danger of the current environmental situation, analysis of environmental risks, and assessment of potential environmental hazards. The described approach allows an integrated assessment of the existing environmental hazard only at a particular area, without taking into consideration the potential threat to other NEO sites adjacent to the dangerous territory.

There is also a methodology for assessing the environmental safety of waste [6], the so-called waste input-output model (WIOS), which makes it possible to identify its potential threat. The use of the WIOS model is illustrated by modeling the overall environmental loads of the wastewater treatment process at an enterprise in Germany. The results show that differences in the composition of waste coming to treatment have a significant impact on the simulated estimates of total environmental stress caused by wastewater treatment. The disadvantage of that model is that it does not take into consideration the concentration of pollutants in waste from other sources.

The methodology for assessing the identification and systematization of existing and potential sources of environmental hazards is worthy of consideration [7]. Determining the toxicity of industrial waste is based on its physical and chemical properties. Undoubtedly, an attempt to develop universal criteria is valuable in the cited procedure. Specifically, a general waste safety index (HP) was proposed, using a new aggregation operator, which was tested in studies of the Kolkata Metropolitan District. However, HP cannot be considered universal because it could only be calculated for one type of waste.

Of scientific interest is a study [8], in which waste toxicity was examined by the estimation method and by testing the simulated geochemical system containing HM for leaching. The estimation method made it possible to determine high concentrations of HM in a wide range of searches for toxic substances. However, the authors do not take into consideration the processes of complex formation and there was no identification of the presence of ions of other toxic elements. Testing for leaching was carried out at a ratio of liquid/solid matter \((L/S)\geq10.000\) in the pH range of 5.5–8.5. Measurements based on leaching tests have been found to be superior to the accuracy calculation method; they, however, appear problematic from a practical and functional point of view.

All above calculation models, given their undeniable scientific value, miss the algorithm of holistic assessment of environmental safety of industrial waste. The reported results [5–8] provide an approximate prediction of the most likely ways of negative impact of waste on NEO. The most important priorities at the current stage of waste research development are to maximally identify the quality and quantity composition of waste, and to detect its toxic components.

Most industrial wastes are complex objects, so various chemical, physical-chemical, and biological research methods are used to assess their toxicity. Choosing any of these methods for a particular research is based on the composition of the waste and the study objectives.

Authors of [9] report experimental data on determining the content, mobility, and phytotoxicity of HM in industrial waste using its chemical characteristic and biological tests. However, the use of biotesting alone in research does not make it possible to provide an objective assessment of waste toxicity parameters, as it is limited by the sensitivity of test objects.

Paper [10] described a comparative analysis of the applicability of chemical, physical-chemical, and biological methods in studies into the toxicity of industrial waste. An enhanced monitoring program was outlined, including the identification of toxic substances and gross, movable, water-soluble forms of toxic elements. However, despite the wide study range discussed in the paper, the issues related to the identification of sanitary and toxicological characteristics of neutralized galvanic sludge (GS) remained unresolved. The reported results cannot be used to fully characterize the environmental safety of this type of waste.

The option to solve above tasks may be the development of a standard procedure for studying industrial waste. This approach was applied in studies [11–13], which consider a comprehensive approach for exploring waste toxicity. Authors of [11, 12] studied the extraction of HM from industrial waste and determined their phytotoxicity. Experimental data on the migration processes of toxic compounds from HS to soils were reported in [13]; their effect on plant objects was established. However, there are no consistent phases for conducting a research that would allow an objective assessment of the technogenic impact exerted by industrial waste on natural environmental objects (NEO).

Thus, in assessing the environmental safety of industrial waste, it is appropriate to devise unambiguous programs to study it. They should have a high expressiveness and greater informativeness, which would enable the identification of toxic compounds in waste in a short period of time and the estimation of their impact on NEO.

3. The aim and objectives of the study

The aim of this study is to construct an algorithm to assess the degree of environmental safety of galvanic waste.

To accomplish the aim, the following tasks have been set:
- to determine the mineral composition of model galvanic sludge;
- to perform a sanitary and chemical assessment of model galvanic sludge;
- to investigate patterns in heavy metal migration in soils contaminated with model galvanic sludge;
- to study the potential phytotoxicity of model galvanic sludge.
4. Materials and methods to study the environmental safety of galvanic sludge

The model galvanic sludge used was the solutions of salts of copper sulfate and zinc. Deposition was carried out in solutions at pH_{pr}=4.5, whose metal ion content is, g/l, \( C_{Zn}^+ = 52.250; C_{Cu}^+ = 59.850 \).

The choice of model solutions and their initial concentration is justified by the actual composition of wastewater from different enterprises. Selecting the copper and zinc metal ions for our study is due to their high degree of toxicity and significant amount in industrial GS.

A reagent method has been chosen to neutralize the model copper-zinc waters, which includes their treatment with slaked lime (Ca(OH)\(_2\)). The GS resulting from the process of neutralization takes the form of a pasty mass of complex and unstable composition of dark gray color.

To determine the composition of GS samples, the diffractograms were acquired from the powder diffractometer “Siemens D500” (Germany) in copper radiation with a graphite monochromator. The full-profile diffractogram is measured at a range of \( 5<2\theta <80^\circ \) in increments of 0.02° and a buildup time of 40 seconds.

The quantification of Cu\(^{2+}\) and Zn\(^{2+}\) in the GS was carried out by a method of electron-probe microanalysis at the scanning electron microscope JSM-6390 LV (Japan).

The degree of phytotoxicity of GS samples on NEO sites was determined by biotesting methods, implying the investigation of the test object’s response to the effects of pollutants. To this end, the system “GS-natural object” was simulated in the laboratory.

The concentrations of Cu\(^{2+}\) and Zn\(^{2+}\) ions in the model environment were determined by the atomic-absorption method at the Saturn spectrophotometer at a wavelength for zinc – 213.9 nm, for copper – 324.8 nm; \( J = 10 \) mA.

5. Results of studying the environmental safety of galvanic sludge

Evaluation of sanitary and toxicological properties of galvanic-produced waste was considered using an example of the model copper-zinc GS, formed after neutralization of spent electrolyte used to etch brass. The sequence of our studies, the methods used, and the main stages of experimental work are presented using an example of the system “GS-natural object”, modeled in the laboratory.

5.1. Determining the mineral composition of galvanic sludge

The elemental composition of GS samples is studied by electron-probe microanalysis. Information about features of the GS crystalline structure is provided by X-ray phase analysis. The method makes it possible to confirm or disprove the phase composition of waste, which was assumed based on our chemical elemental analysis. Full-profile diffractograms are measured at a specific angle interval with a fixed step and accumulation time. The initial phase search is performed based on the PDF-1 file, followed by calculation of roentgenograms according to the Rietveld method, employing the software FullProf. 98.

**Example.** Electron-probe and X-ray tests were carried out to identify the nature of the crystalline phases and to determine the composition of the model copper-zinc GS. The elemental composition of the sediment sample, according to the electron-probe microanalysis, is, %: Cu – 25.46; Zn – 17.92; Ca – 10.3; O – 33.74; S – 12.58. The X-ray phase analysis of a sample of the model GS revealed that its main phases are gypsum CaSO\(_4\)·2H\(_2\)O, gunningite ZnSO\(_4\)·H\(_2\)O, bassanite CaSO\(_4\)·0.5H\(_2\)O, ktenasite (ZnCu\(_3\))(SO\(_4\)\(_3\))(OH)\(_2\)(H\(_2\)O)\(_{12}\), antlerite Cu\(_3\)(OH)\(_3\)(SO\(_4\)), goslarit ZnSO\(_4\)·7H\(_2\)O, and namuvit (Zn\(_{12}\)Cu\(_{6}\)\(_3\))(SO\(_4\))\(_3\)(OH)\(_6\)·4H\(_2\)O.

Determining the mineral composition of galvanic sludge makes it possible to identify minerals containing HM, which, in long-term interaction with the environment, could form easily soluble toxic compounds. The presence of such compounds in the sludge composition determines the migration and biological activity of its components.

5.2. Sanitary and chemical assessment of galvanic sludge

In order to quantify the migration of HM ions from galvanic sludge to the environments in contact with them (soil and water), a sanitary and chemical assessment of GS is carried out. The forms of HM ions bonds are determined in the analysis of three types of extracts obtained using extractants: distilled water; acetate-ammonium buffer solution, and mineral acid (0.8 M HCl). The extracts are produced by mixing GS with an extractant at a ratio of 1:10, followed by aging at 20 °C, settling and filtering through a paper filter. The concentrations of HM in aluates are determined by the atomic-absorption method in 1, 3, 7, 10, 20 and 30 days.

**Example.** After neutralization, GS are toxic due to the presence of insoluble HM compounds in them. Therefore, to study the effects of the GS contact with the external environment, an experimental simulation of the behavior of the system “GS-model environment” was carried out. The research results are given in Table 1.

| HM                  | Time of dissolution of copper-zinc GS, days |
|---------------------|--------------------------------------------|
| Zn\(^{2+}\)         | 6.85                                       |
| Cu\(^{2+}\)         | 6.48                                       |
| Acetate-ammonium buffer solution (pH=5.1) |
| Zn\(^{2+}\)         | 2.26                                       |
| Cu\(^{2+}\)         | 1.17                                       |
| Distilled water (pH=6.8) |
| Zn\(^{2+}\)         | 1.28                                       |
| Cu\(^{2+}\)         | 0.02                                       |

Gunningite ZnSO\(_4\)·H\(_2\)O and goslarit ZnSO\(_4\)·7H\(_2\)O from the model GS have good solubility in water and prede-
termind the emergence of Zn$^{2+}$ ions in the water solution. Weak solubility in water, but good solubility in antlerite acids $\text{Cu}_2(\text{OH})_3(\text{SO}_4)_2$, explains the presence of Cu$^{2+}$ ions in acid extracts. The presence of Cu$^{2+}$ and Zn$^{2+}$ in acid and acetate-ammonium buffer extracts is associated with hydrated double hydroxy salts – namuvit (Zn$_{3.2}$Cu$_{0.8}$SO$_4$)(OH)$_6$·4H$_2$O and ktenasit (ZnCu$_4$(SO$_4$)$_2$(OH)$_2$(H$_2$O)$_2$).

The dissolution of copper and zinc compounds in distilled water and acetate-ammonium buffer solution has a similar upward dynamic, indicating the similarity of the occurring processes. In water extracts, Cu$^{2+}$ ions have a small proportion of water-soluble forms compared to Zn$^{2+}$. And in the solution of acetate-ammonium buffer both metals are characterized by high concentrations of movable forms extracted from GS. The emission of Cu$^{2+}$ and Zn$^{2+}$ ions from the samples of GS into acid extracts is much higher than that into aquatic and acetate-ammonium. In the first day, the concentrations of HM ions in acid extracts increase by 1.11–1.21 times. Longer exposure (30 days) of GS to acid environment does not lead to a further increase in the concentration of ions.

Sanitary and chemical assessment of galvanic sludge makes it possible to determine the structure and orderliness of the presence of HM in GS, the degree of dissolution of GS in solutions of a certain acidity and characterize their environmental safety.

5.3. Studying patterns of heavy metal migration in soils when they are contaminated with galvanic sludge

The specificity of anthropogenic transformation of heavy metals in the system “GS-soil” is defined by the ratio of external and internal factors of HM migration: the first include the physical and chemical properties of soils, the second – the physical and chemical properties of HM themselves, as well as and their ability to dissolve. In the laboratory, models of soil layers, on top of which is a constantly moist layer of GS, are created in order to study the migration of HM from GS to soil. To do this, plastic pipes with a diameter of 0.35 m and a height of 1 m are filled with pre-dried soils. The upper surface of each soil column holds shredded GS, which, over six months, is irrigated with distilled water under a mode corresponding to natural moistening.

Patterns in the migration and distribution of HM in soils are investigated in selected samples of soil layers, cm: 0–5, 10–15, 20–25, 50–75, 100. The method of atomic-absorption spectrometry is applied to determine the content of HM in each soil layer. Soil pollution levels are computed based on the accumulation rate ($K_i$)

$$K_i = \frac{C_i}{C_b},$$

where $C_i$ is the concentration of a metal ion in soil, $C_b$ is the concentration of a metal ion in the background (control) soil sample.

**Example.** Patterns in HM migration and their distribution in soils, pre-contaminated by GS, are studied in soil samples – black earth typical, medium-washed, loamy (BTML); meadow-black-earth, light-loamy (MBL); meadow alluvial sandy loam (MAS), sod-podzolized cohesive sand (SPC). Experimental data on the system “GS-soil” are given in Table 2.

| Indicator | Background sample | Soil layer, cm |
|-----------|-------------------|----------------|
|           | 0–5   | 10–15 | 20–25 | 50–75 | 100 |
| $K_i$(Zn) | 73.51 | 0.52  | 0.81  | 0.63  |
| $K_i$(Cu) | 5.21  | 0.81  | 0.72  | 1.12  |
| pH        | 7.66  | 8.12  | 8.27  | 8.31  |
| LC$_s$(Cu)| 7.11  | 3.54  | 5.75  | 4.87  | 7.08 |
| LC$_s$(Zn)| 3.13  | 229.3 | 7.53  | 2.39  | 1.73 |

Note: LC$_s$ [3] calculated as the ratio of Cu$^{2+}$ and Zn$^{2+}$ concentrations in contaminated soils to their LC. LC$_s$(Cu)=3 mg/kg; LC$_s$(Zn)=23 mg/kg, respectively.

5.4. Determining the potential phytotoxicity of galvanic sludge

Experiments on the influence of HM, contained in contaminated soils, on plant objects under controlled conditions could determine the impact of external negative factors on the stability of plant development and adaptation to them. In the laboratory, studying the phytotoxicity of GS involves HM-contaminated layers of soils, received at the previous stage 4, from a depth of, cm, 0–5, 10–15, 20–25, 50–75, 100. The selected soil is dried in the open air until the permanent weight is reached. Air-dry soil weighing 1,500 g is introduced in containers with a diameter of 0.09 m and a height of 0.15 m. Seeds in the quantity of 15 pieces are planted in
The effect of copper and zinc ions in the group of medium-absorbing metals affect the bio-objects of test plants under conditions of model soil pollution with anthropogenic contamination. The main growth indicators of seed germination (cress and oats) under controlled conditions have been investigated. The main growth indicators of seed germination of test plants under conditions of model soil pollution with HM are given in Table 3.

As shown by data in Table 3, the Cu$^{2+}$ and Zn$^{2+}$ ions from BTML make it possible to assess the danger of GS as one type of industrial waste.

6. Discussion of results of studying the environmental safety of galvanic sludge

The results of research into the environmental safety of galvanic sludge show that, due to its high toxicity, industrial galvanic waste is a global issue in environmental design. The methods used in the study and the main stages of experimental work make it possible to assess the danger of GS as one type of industrial waste.

The reported data (subchapter 5.2) have not only made it possible to establish the elemental and mineral composition of the derived GS, but also showed that the process of neutralization of sulfate copper-zinc solutions with lime milk proceeds in two stages. First stage: calcium ions react with sulfate-ion formations of semi-aquatic and two-water gypsum, falling out in the form of sediment as a result of reaction

$$SO_4^{2-} + Ca(OH)_2 + 2H^+ \rightarrow CaSO_4 - 0.5H_2O \rightarrow CaSO_4 - 2H_2O.$$
Stage two: heavy metal compounds are formed

\[ 3\text{CuSO}_4 + 2\text{Ca(OH)}_2 \rightarrow \text{Cu}_2(\text{OH})_3(\text{SO}_4) + 2\text{CaSO}_4 \]

The concentration of OH ions in the solution is not sufficient to form copper and zinc hydroxides, which is why aqua-complexes are formed, \( \text{ZnSO}_4 \cdot 3\text{H}_2\text{O} \), \( \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \), and aqua-hydro-complexes (\( \text{ZnCu}_3(\text{SO}_4)_6(\text{OH})_2(\text{H}_2\text{O})_2 \), \( \text{Cu}_3(\text{OH})_4(\text{SO}_4)_2 \), (\( \text{Zn}_3\text{Cu}(\text{OH})_6(\text{SO}_4)_3(\text{OH})_6 \cdot 4\text{H}_2\text{O} \)).

According to the research results given in Table 1, it was established that the ions included in HM composition (\( \text{Cu}^{2+} \) and \( \text{Zn}^{2+} \)) have high water-migration activity. Of the two metals studied in the model GS, zinc is easier to release ions into the solution than copper, so the \( \text{Zn}^{2+} \) cations contribute more to the negative impact on NEO than the \( \text{Cu}^{2+} \) cations.

As shown by experimental data in Table 2, the greatest accumulation of \( \text{Cu}^{2+} \) and \( \text{Zn}^{2+} \) is noted in the upper horizons of the soils studied, where the greatest anthropogenic pollution of GS occurs. The intensity of transformation of the \( \text{Cu}^{2+} \) and \( \text{Zn}^{2+} \) ions from GS to soil increases in a series: BTML<MBL<MAS<SPC.

The reaction of the soil environment is the driving factor in dissolving \( \text{Cu}^{2+} \) and \( \text{Zn}^{2+} \) from GS and their transformation into soil. In the soils under study, the greatest mobility of \( \text{Cu}^{2+} \) and \( \text{Zn}^{2+} \) in soils with \( \text{pH} > 7 \) is noted. The presence of phytohormonal processes is explained by the high balance of nutrient reserves in the plants themselves and their migration from the soils into the plants.

The disadvantage of this research is that the series of laboratory tests was performed on the model GS, which is undoubtedly different from the actual waste from galvanic production. At the same time, the results obtained could be applicable to assess the degree of environmental safety of other industrial wastes.

Promising areas of further research is the study into the impact of GS of another composition, for example, three-component, on NEOs. In addition, a priority is to find ways to assess the environmental safety of industrial waste, specifically the sludge from galvanic production.

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**Fig. 1.** Block diagram of the algorithm for assessing the environmental safety of copper-zinc GS
7. Conclusions

1. The mineral composition of GS has been determined. Minerals containing HM have been identified, ZnSO₄·H₂O, ZnSO₄·7H₂O, Cu₅(OH)₄(SO₄), (Zn₂Cu₁₀,₈) (SO₄)(OH)·4H₂O, which, in long-term interaction with the environment, could form easily soluble toxic compounds. It has been established that the process of neutralizing sulfate copper-zinc solutions with lime milk proceeds in two stages: the formation of semi-aquatic and two-water gypsum; the formation of HM compounds.

2. A sanitary and chemical assessment of the model galvanic sludge was carried out. It has been established that the emission of Zn²⁺ ions from GS samples to eluates is much higher than Cu²⁺. Therefore, of the two metals studied in the model GS, the Zn²⁺ cations contribute more to the negative impact on NEO compared with Cu²⁺ cations.

3. The processes of migration and distribution of HM ions in the system “GS-soil” have been investigated. The series of intensity in the transformation of Cu²⁺ and Zn²⁺ ions from GS to soil have been established: BTML<MBL<MAS<SPC. It has been proven that the mobility of HM ions depends on the acidity of the soil. For example, for Zn²⁺, the maximum mobility is observed in soils with pH=7.

For Cu²⁺, mobility in neutral or alkaline soils is lower than in acidic soils.

4. The quantitative indicators of potential phytotoxicity of GS have been defined: germination, energy, friendliness and duration of germination of test plant seeds. It has been shown that the joint effect of Cu²⁺ and Zn²⁺ manifests itself both in inhibition and in stimulating the growth processes of test plants, and is determined first of all, by the biological specificity of the test culture itself, as well as the properties of the soil and the degree of its contamination. The LC₅₀ indicators have been established for the ions of Cu²⁺ and Zn²⁺ in the soils under study, which contribute to the stimulation of the development of test plants.

For SPC:
- for watercress LC₅₀(Cu)=0.8, LC₅₀(Zn)=0.3,
- for oats LC₅₀(Cu)=1.4 – 2.0; LC₅₀(Zn)=0.7 – 12.1;
- for MAS:
- for watercress LC₅₀(Cu)=0.5 – 1.1, LC₅₀(Zn)=0.3,
- for oats LC₅₀(Cu)=0.6 – 1.1, LC₅₀(Zn)=0.1 – 23.4;
- for MBL:
- for watercress LC₅₀(Cu)=1.1 – 1.8, LC₅₀(Zn)=0.3,
- for oats LC₅₀(Cu)=0.9 – 3.3, LC₅₀(Zn)=0.3 – 114.6;
- for BTML:
- for watercress LC₅₀(Cu)=7.1, LC₅₀(Zn)=1.7,
- for oats LCₕ(Cu)=5.5 – 36.6, LC₅₀(Zn)=1.6 – 229.3.

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