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

На підставі розробленого алгоритму оцін-ки санітарно-токсикологічних властивостей системи «Гальваношлам – природний об'єкт» з використанням модельного мідно-цинково-го шламу. Ідентифіковано мінерали гальва-ношламу, що містять іони важких мета-лів – $ZnSO_4 \cdot H_2O$, $ZnSO_4 \cdot 7H_2O$, $Cu_3(OH)_4(SO_4)$, $(Zn_{3.2}Cu_{0.8})(SO_4)(OH)_6 \cdot 4H_2O$, які при тривалій взаємодії з навколишнім середовищем можуть утворювати легкорозчинні токсичні спо-луки. Встановлено, що процес нейтралізації сульфатних мідно-цинкових розчинів вапня-ним молоком протікає в два етапи: утворен-ня полуводного і двуводного гіпсу; утворення сполук важких металів. Вивчена водно-мігра-ційна активність іонів Cu^{2+} і Zn^{2+}, які входять до складу гальваношламу. Доведено, що з двох досліджуваних металів катіони Zn^{2+} вносять більший внесок в негативний вплив на об'єк-ти довкілля в порівнянні з катіонами Cu^{2+}. Досліджено особливості розподілу і міграції іонів важких металів у ґрунтах після забруд-нення їх гальваношламом. Встановлено, що інтенсивність трансформації іонів Zn^{2+} та Cu^{2+} з гальваношламів до ґрунту визначаєть-ся типом ґрунту і фізико-хімічними властиво-стями самих металів. Встановлена кореляція між рухливістю іонів важких металів і кис-лотністю ґрунтів. Для Zn^{2+} максимальна рух-ливість спостерігається в ґрунтах з $pH \approx 7$. Для Cu^{2+} рухливість в нейтральних або лужних ґрунтах нижча, ніж у ґрунтах з кислим сере-довищем. Визначено основні кількісні показни-ки потенційної фітотоксичності гальваношла-му – всхожість, енергія, дружність і три-валість проростання насіння тест-рослин. Показано, що сумісна дія Cu^{2+} і Zn^{2+} прояв-ляється як в інгібуванні, так і в стимулюванні ростових процесів тест-рослин і визначаєть-ся, перш за все, біологічною специфікою самої тест-культури, а також властивостями ґрунту і ступенем їх забруднення.

Представлений в роботі порядок виконання досліджень дозволяє прогнозувати небезпеку гальваношламів для навколишнього природно-го середовища. А також, може бути засто-сований природоохоронними і проектними організаціями при проведенні агроекологічного моніторингу

Ключові слова: алгоритм, відходи виробни-цтва, гальваношлам, санітарно-токсикологіч-ні властивості, екологічна безпека

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1. Introduction

One of the most pressing environmental issues for indus-trial enterprises, which employ galvanic processes in their technological cycle, is the problem of accumulation of gen-erated waste, so-called galvanic sludge (GS) [1, 2]. GS con-taining 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 meth-odological 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)$\geq$10.000 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 $pH_{prim.}$=4.5, whose metal ion content is, g/l, $C^0_{Cu^{2+}} = 52.250$; $C^0_{Zn^{2+}} = 59.850$.

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 $5<2\theta<80°$ 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 deter-

mine 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 $CaSO_4 \cdot 2H_2O$, gunningite $ZnSO_4 \cdot H_2O$, bassanite $CaSO_4 \cdot 0.5H_2O$, ktenasite $(ZnCu)_5(SO_4)_4(OH)_{12}(H_2O)_{12}$, antlerite $Cu_3(OH)_4(SO_4)$, goslarit $ZnSO_4 \cdot 7H_2O$, and namuvit $(Zn_{3.2}Cu_{0.8})(SO_4)(OH)_6 \cdot 4H_2O$.

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.

Table 1

Dissolution of HM compounds in the system "GS-model environment"

HM	Time of dissolution of copper-zinc GS, days					
	1	3	7	10	20	30
Concentration of metal ions (C), g/l						
0.8 M HCl (pH=1.98)						
Zn^{2+}	6.85	7.36	7.39	7.28	6.74	6.58
Cu^{2+}	6.48	7.28	7.35	7.33	7.28	7.25
Acetate-ammonium buffer solution (pH=5.1)						
Zn^{2+}	2.26	2.79	3.42	4.05	5.38	5.87
Cu^{2+}	1.17	1.39	1.62	1.80	1.96	2.54
Distilled water (pH=6.8)						
Zn^{2+}	1.28	3.33	3.47	3.71	3.79	4.18
Cu^{2+}	0.02	0.03	0.04	0.04	0.06	0.08

Gunningite $ZnSO_4 \cdot H_2O$ and goslarit $ZnSO_4 \cdot 7H_2O$ from the model GS have good solubility in water and prede-

termined the emergence of Zn^{2+} ions in the water solution. Weak solubility in water, but good solubility in antlerite acids $Cu_3(OH)_4(SO_4)$, 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 hydroxo salts – namuvit $(Zn_{3.2}Cu_{0.8})(SO_4)(OH)_6·4H_2O$ and ktenasit $(ZnCu)_5(SO_4)_4(OH)_{12}(H_2O)_{12}$.

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_c)

$$K_c = \frac{C}{C_b}, \tag{1}$$

where C 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.

Table 2

Key experimental data in the system "GS-soil"

Indicator	Back-ground sample	Soil layer, cm				
		0÷5	10÷15	20÷25	50÷75	100
BTML						
$K_c(Zn)$	–	73.51	2.38	0.52	0.81	0.63
$K_c(Cu)$	–	5.21	0.92	0.81	0.72	1.12
pH	8.71	7.66	8.12	8.12	8.27	8.31
$LC_s^{'}(Cu)$	7.11	36.58	5.54	5.75	4.87	7.08
$LC_s^{'}(Zn)$	3.13	229.3	7.53	1.59	2.39	1.73
MBL						
$K_c(Zn)$	–	657.12	187.33	14.52	1.73	1.52
$K_c(Cu)$	–	33.91	2.12	1.91	1.22	2.01
pH	6.91	5.16	5.47	5.91	6.13	6.21
$LC_s^{'}(Cu)$	0.89	3.29	1.84	1.69	1.09	1.81
$LC_s^{'}(Zn)$	0.17	114.6	32.65	2.53	0.32	0.26
MAS						
$K_c(Zn)$	–	423.31	259.12	99.84	9.33	1.92
$K_c(Cu)$	–	13.53	1.92	0.91	1.02	1.01
pH	7.62	6.41	6.12	5.93	6.21	6.36
$LC_s^{'}(Cu)$	0.57	7.73	1.12	0.51	0.61	0.62
$LC_s^{'}(Zn)$	0.08	33.5	23.35	7.9	0.74	0.15
SPC						
$K_c(Zn)$	–	77.81	43.53	38.82	14.13	2.31
$K_c(Cu)$	–	9.62	1.94	2.34	2.21	2.62
pH	5.31	4.41	4.30	4.21	4.21	4.51
$LC_s^{'}(Cu)$	0.75	7.18	1.36	1.68	1.68	1.93
$LC_s^{'}(Zn)$	0.28	21.65	12.12	10.81	3.93	0.65

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

Studying patterns in heavy metal migration in soils when they are contaminated with galvanic sludge makes it possible to characterize the specificity of HM anthropogenic transformation in the system "GS-soil".

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

each container at a depth of 0.01 m. The seed is sprouted at a temperature of 20 °C.

To assess the impact of soil contamination with HM on seed germination, the following indicators are used: germination, energy, friendliness, and duration of germination.

Germination (G) is the number of seeds that have sprouted in the first 7 days of germination, %.

Germination energy (E) is the number of seeds that have sprouted in the first 3 days of germination, %.

Germination friendliness (F) is the average percentage of seeds sprouted in the 1st day of germination, %.

$$F = \frac{D}{A}, \tag{2}$$

where D is full germination, %; A is the number of days of germination.

Duration of germination (C) is the average duration of germination per seed, day

$$C = \frac{(a \cdot 1) + (b \cdot 2) + (d \cdot 3) + \ldots}{(a + b + d + \ldots)}, \tag{3}$$

where a is the number of seeds that have sprouted in the 1st day; b is the number of seeds that have sprouted in 2 days; d is the number of seeds that have sprouted in 3 days, etc.

Example. The effect of copper and zinc ions in man-made-contaminated soils on test plant seeds (watercress and oats) under controlled conditions has 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 the group of medium-absorbing metals affect the bio-objects

tested, causing changes in their development. Thus, the stimulation of plant growth is observed in the first 7 days. However, with the increase in the growing time to 30 days, the dynamics in the development of test plants changes. In the period 7–30 days, oats demonstrated the stimulating effect of sprouts development, sprouts of watercress – depressing. That is, the seeds of test plants, having at the initial developmental stages the sufficient potential of nutrients, are able to suppress the oppressive action of HM ions. However, as the growing period increases, the negative impact of toxic metals increases.

Determining the potential phytotoxicity of galvanic sludge makes it possible to establish the influence of HM galvanic sludge on plant growth and development indicators and is important in agroecological monitoring.

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

The results of research into the environmental safety of waste 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 with the formation of semi-aquatic and two-water gypsum, falling out in the form of sediment as a result of reaction
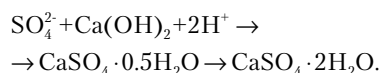
$$SO_4^{2-} + Ca(OH)_2 + 2H^+ \rightarrow$$
$$\rightarrow CaSO_4 \cdot 0.5H_2O \rightarrow CaSO_4 \cdot 2H_2O.$$

Table 3

Main growth indicators of seed germination of test plants under conditions of model soil pollution with HM

Indicator	background		contaminated soil layer, cm									
			5		10÷15		20÷25		50÷75		100	
	water-cress	oats	water-cress	oats	water-cress	oats	water-cress	oats	water-cress	oats	water-cress	oats
BTML												
$E, \%$	27.3	13.3	24.2	73.3	27.2	73.3	37.1	66.7	40.2	56.7	49.1	60.1
$G, \%$	27.4	33.3	40.1	100	20.1	100	27.2	86.7	30.1	73.3	45.2	93.3
$F, \%$	6.8	20.2	3.4	25.1	6.8	25.1	4.0	21.7	5.7	16.1	7.1	13.3
$C, \%$	4.0	7.0	3.2	4.0	2.2	3.4	2.9	3.5	4.0	3.9	6.0	5.2
MBL												
$E, \%$	13.2	100	–	16.7	–	83.3	31.2	80.1	42.2	73.3	47.1	77.8
$G, \%$	13.1	100	–	70.1	–	86.7	22.1	86.7	27.1	93.3	42.1	100
$F, \%$	1.3	33.3	–	7.3	–	21.7	3.1	14.4	4.2	18.7	4.7	16.7
$C, \%$	1.2	2.5	–	5.6	–	3.1	1.9	3.0	5.2	3.6	2.4	3.2
MAS												
$E, \%$	7.2	60.1	9.1	71.1	24.2	100	27.1	88.9	27.3	88.9	11.2	86.7
$G, \%$	7.3	66.7	11.1	100	28.1	100	25.2	100	22.1	100	22.1	100
$F, \%$	1.8	11.1	0.5	14.3	0.2	33.3	0.2	25.3	1.5	20.1	1.9	13.3
$C, \%$	1.1	4.2	1.2	4.1	3.4	2.7	2.8	3.2	2.9	3.8	4.4	2.7
SPC												
$E, \%$	100	53.3	–	71.1	–	84.4	9.2	71.1	9.1	77.8	2.3	57.8
$G, \%$	73.1	66.7	–	100	–	100	9.1	77.8	9.2	93.3	16.1	86.7
$F, \%$	25.2	13.3	–	16.6	–	20.2	1.3	20.1	1.3	25.1	1.8	12.5
$C, \%$	16.1	2.8	–	4.3	–	3.7	0.3	3.1	1.2	3.8	0.7	5.9

Stage two: heavy metal compounds are formed

$$3CuSO_4 + 2Ca(OH)_2 \rightarrow Cu_3(OH)_4(SO_4) + 2CaSO_4\downarrow.$$
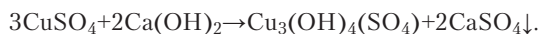
The concentration of OH ions in the solution is not sufficient to form copper and zinc hydroxides, which is why aqua-complexes are formed, $ZnSO_4 \cdot H_2O$, $ZnSO_4 \cdot 7H_2O$, and aqua-hydro-complexes $(ZnCu)_5(SO_4)_4(OH)_{12}(H_2O)_{12}$, $Cu_3(OH)_4(SO_4)$, $(Zn_{3.2}Cu_{0.8})(SO_4)(OH)_6 \cdot 4H_2O$.

According to the research results given in Table 1, it was established that the ions included in HM composition (Cu^{2+} and 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 Zn^{2+} cations contribute more to the negative impact on NEO than the Cu^{2+} cations.

As shown by experimental data in Table 2, the greatest accumulation of Cu^{2+} and 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 Cu^{2+} and 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 Cu^{2+} and Zn^{2+} from GS and their transformation into soil. In the soils under study, the mobility of Cu^{2+} and Zn^{2+} ions increases with lower pH (Table 2), and the alkaline environment of soils contributes to the transition of Cu^{2+} and Zn^{2+} to a stationary state. Thus, the low-alkaline BTML environment helps anchor soil particles of HM ions, so there is the least migration. It should be noted that the mobility of Cu^{2+} ions is higher in soils with pH≥7, and that of the Zn^{2+} ions – in soils with pH≈7.

The HM ions, depending on their concentration in soils, could have both stimulating and depressing effects on plant development. This relationship is proved by the comparative analysis between the soils contaminated with HM (Table 2) and the growth rates of test plants (Table 3). Thus, $LC_s^{'}$ indicators were established for the ions of Cu^{2+} and Zn^{2+} in the soils under study, which contribute to the stimulation of the development of test plants.

For SPC:
for watercress $LC_s^{'}(Cu)=0.8$, $LC_s^{'}(Zn)=0.3$,
for oats $LC_s^{'}(Cu)=1.4-2.0$; $LC_s^{'}(Zn)=0.7-12.1$;
for MAS:
for watercress $LC_s^{'}(Cu)=0.5-1.1$, $LC_s^{'}(Zn)=0.3$,
for oats $LC_s^{'}(Cu)=0.6-1.1$, $LC_s^{'}(Zn)=0.1-23.4$;

for MBL:
for watercress $LC_s^{'}(Cu)=1.1-1.8$, $LC_s^{'}(Zn)=0.3$,
for oats $LC_s^{'}(Cu)=0.9-3.3$, $LC_s^{'}(Zn)=0.3-114.6$;
for BTML:
for watercress $LC_s^{'}(Cu)=7.1$, $LC_s^{'}(Zn)=1.7$,
for oats $LC_s^{'}(Cu)=5.5-36.6$, $LC_s^{'}(Zn)=1.6-229.3$.

Physiological and biochemical processes occurring in the plants themselves are the cause of the difference in their development. Thus, the high balance of nutrient reserves in the presence of phytohormonal processes is explained by the higher rates of germination, energy, friendliness and duration of germination in the seeds of oat in comparison with similar indicators for watercress.

In the course of our research, we constructed an algorithm to study the environmental safety of GS, which includes: the identification of chemical composition, detection of soluble minerals, assessment of migration, biological activity and phytotoxicity of HM ions, incoming from GS to soil. An example of the application of an algorithm to assess the environmental safety of copper-zinc GS is given by a block diagram (Fig. 1).

The advantage of the constructed algorithm to assess the degree of environmental safety of GS is its simplicity and the use of non-expensive equipment, as evidenced by the examples. In contrast to existing procedures, the proposed research algorithm makes it possible to conduct a comprehensive assessment of the impact of GS on NEO sites. Therefore, the probabilistic forecast of the GS danger for a NEO based on the proposed results could be applied by environmental and design organizations in agricultural-ecological monitoring.

Our research was limited to the study of soluble components of GS and did not take into consideration the effects of insoluble compounds contained in GS on NEO sites.

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.
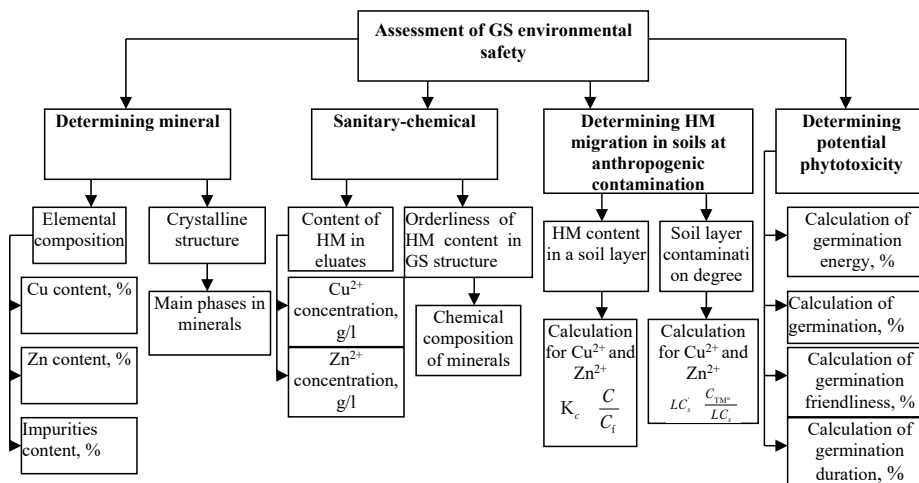

Fig. 1. Block diagram of the algorithm for assessing the environmental safety of copper-zinc GS

7. Conclusions

1. The mineral composition of GS has been determined. Minerals containing HM have been identified, $ZnSO_4 \cdot H_2O$, $ZnSO_4 \cdot 7H_2O$, $Cu_3(OH)_4(SO_4)$, $(Zn_{3.2}Cu_{0.8})(SO_4)(OH)_6 \cdot 4H_2O$, 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 Zn^{2+} ions from GS samples to eluates is much higher than Cu^{2+}. Therefore, of the two metals studied in the model GS, the Zn^{2+} cations contribute more to the negative impact on NEO compared with Cu^{2+} 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 Cu^{2+} and Zn^{2+} 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 Zn^{2+}, the maximum mobility is observed in soils with pH≈7. For Cu^{2+}, 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 Cu^{2+} and Zn^{2+} 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 $LC_s^{'}$ indicators have been established for the ions of Cu^{2+} and Zn^{2+} in the soils under study, which contribute to the stimulation of the development of test plants.

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

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