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Emission of Heavy Metals from Galvanic Production Sludge in Water Objects and Soil

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Abstract---*Galvanic sludgeis a waste hazardous to the environment. The composition of galvanic sludge generated in various industries is much diversified, but galvanic sludge contains heavy metal ions as harmful pollutants. Upon that, the content of heavy metal ions in the aqueous extract reflects the mobility degree of elements in the soil, and in the case of the ammonium acetate extract, it reflects the total content of potentially hazardous elements that can, through the transition to the mobile form, have a negative impact on environmental objects. The content of heavy metal ions in the aqueous extract and the extract of the galvanic sludge-acetate ammonia buffer was determined by atomic emission spectroscopy. A series of elements by mass content in an aqueous extract is Si, Mo, Cu, Zn, Cr, B, Fe, Ni, Co, Sb, Se.A series of elements by mass content in the acetate-ammonium extract is Zn, Si, Mo, Cu, Cr, Fe, B, Mn, Ni, Sr, Co, Al, Se, Sb, Ba. Due to the high solubility of most galvanic sludge, pollutant pollutants are relatively easily washed into the water phase and pollute water bodies and the environment. The prior polluting heavy metals in the mobile form are in the order of decreasing values: Mo, Cu, Zn and Cr, which account for more than 99% of the pollution of the aqueous phase with galvanic production sludge. The neutralization of sludge with regard heavy metals is possible when converted to insoluble forms or removed from the sludge, especially such elements as Mo, Cu, Zn, Cr, Co, Ni.*

Keywords--- *Galvanic Sludge, Phosphate Coating, Heavy Metals, Waste, Wastewater.*

I. INTRODUCTION

Electroplated coatings are in demand and are applied in many industries. However, galvanic production is 1 of the sources of environmental pollution by harmful substances and, primarily, heavy metals.

Galvanic wastewater is toxic, as it contains harmful impurities of heavy metals, inorganic acids and alkalis, surfactants and other highly toxic compounds [1]. Solid wastes generated in various galvanic industries contain heavy metals in sparingly soluble form.

The formation and accumulation of galvanic sludge is a major environmental problem, since this industrial waste is a by-product of galvanic production resulting from wastewater treatment and, due to its toxicity, belongs to hazard classes II-III [2].

This waste poses a potential storage hazard due to the toxicity of heavy metal ions contained in sludge and their marked solubility, which can lead to the release of heavy metal ions and their further migration to the soil, groundwater and the environment as a whole. In view of this, the placement of sludge in landfills of solid household

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waste is unacceptable; special landfills eliminating the emission of heavy metals into the environment are required for their disposal. Due to the lack or absence of specially equipped landfills for storing sludge from galvanic production, the majority of enterprises have practically exhausted the possibility of disposing these wastes on their territory. The severity of this problem is due to the lack of cost-effective methods of processing mixed galvanic sludge and environmentally friendly methods for their disposal

The environmental hazard of galvanic sludge can be reduced by the transfer of mobile or soluble forms of toxic pollutants into insoluble forms. In any case, both for assessing the danger of galvanic sludge and for choosing ways to reduce their toxicity, a qualitative and quantitative analysis of galvanic sludge is needed to determine the content of their moving and water-soluble forms of pollutants.

II. METHODS

An aqueous extract for analysis was prepared by dissolving 30 g of a sample of galvanic sludge in 150 ml of water. Then the suspension was treated in a shaker for 30 minutes, after that it was pooled and filtered. In a similar way, an extract from the galvanic sludge was prepared with an acetate-ammonium buffer, with the help of which more heavy metal ions in comparison with a conventional aqueous extract can be transferred to the liquid phase [3, 4].

The pH values of the solutions were measured using the ANION 4100 ionomer. Mineralization was measured using an ANION-7020 conductometer [5].

The content of heavy metal ions was determined by inductively coupled plasma atomic emission spectrometry on an Agilent 720-OES spectrometer [6, 7, 8].

III. RESULTS AND DISCUSSION

Galvanic sludge is a solid powdery mass of light brown colour (Fig. 1). The moisture content in the sample is negligible and equal to 0.1%.

Figure 1: Sludge of Galvanic Production

Most of the galvanic sludge substance is dissolved in water. The share of the insoluble part is relatively small and amounts to 11.3%.

In an aqueous extract, pH, mineralization (Table 1), and the content of heavy metal ions (Table 2) were determined.

For comparison purposes, Table 1 shows the maximum permissible concentration in water bodies with water for drinking and household purposes ($TLV_{drinking\ water}$), the maximum permissible concentration of a pollutant in the water of fishery ponds ($TLV_{open\ reservoirs}$), permissible concentrations of pollutants in wastewater waters allowed for discharge into a centralized wastewater system ($LV_{wastewater.}$)[9].

Table 1: Indices of galvanic sludge aqueous extract

index	*concentration.*	$TLV_{drinking\ water}$	$TLV_{open\ reservoirs}$	$LV_{wastewater}$
pH, units pH	11.3	6.0-9.0	6.5-8.5	6.0-9.0
mineralization by NaCl, mg / dm^3	42350	1000	1000	3000

The pH value of 11.3 indicates the alkaline environment of the aqueous extract, which is the result of the specificity of the galvanic production process. The high alkalinity of the sample means the danger of this waste to the environment since the pH standard for drinking and household water bodies, water bodies of commercial fishing importance and wastewater is within the range of 6-9 pH units (table 1).

The relative mineralization of the galvanic sludge aqueous extract by sodium chloride (NaCl) exceeds the water standard values for water bodies with drinking and household water, as well as reservoirs of commercial fishing importance in more than 40 times, and wastewater in 14 times. It is easy to assume that galvanic sludge contains a large amount of salts and substances of a basic nature.

Therefore, the measurement results are shown in table 1 cause an additional need to measure the content of heavy metal ions in the extract from the sludge galvanic production.

The results of determining the content of heavy metal ions in the aqueous extract and in the extraction of acetate-ammonium buffer and reference data on the standards are shown in table 2.

Table 2: Content of heavy metal ions in the aqueous extract galvanic sludge, the content of heavy metal ions in the extract by ammonium-acetate buffer, standard values

Element	*Concentration in aqueous extract. mg / dm^3*	*Concentration in extract by acetate-ammonium buffer, mg / dm^3*	$TLV_{drinking\ water}$	$TLV_{open\ water\ bodies}$	$LV_{waste\ water}$
Al	<0.1	0.725	0.2	0.04	3
Ba	<0.03	0.018	0.7	0.74	-
Be	<0.01	<0.01	0.0002	0.0003	-

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Cd	<0.05	<0.05	0.001	0.005	0.015
Co	0.151	0.973	0.1	0.01	-
Cr	2.97	24.3	0.05	0.02	0.5
Cu	11.7	144	1	0.001	0.5
Fe	1.33	12.7	0.3	0.05	3
Mn	<0.03	2.22	0.1	0.01	1
Mo	104	253	0.25	0.001	-
Ni	0.154	1.93	0.1	0.01	0.25
Pb	<0.8	<0.8	0.01	0.006	0.25
Sb	0.079	0.122	0.05	0.005	-
Se	0.014	0.449	0.01	0.002	-
Si	160	417	10	-	-
Sr	<0.01	1.24	7	0.4	2
Ti	<0.1	<0.1	0.1	0.06	-
V	<0.2	<0.2	0.1	0.001	-
Zn	3.47	457	1	0.01	1
B	1.63	5.50	0.5	0.5	-
Ag	<0.3	<0.3	0.05	-	-
Tl	<1.5	<1.5	0.0001	-	-
As	<1	<1	0.01	0.05	0.01

To assess the environmental impact of galvanic sludge on water objects by washing heavy metal ions with water and an acetate-ammonium buffer, and concentration coefficients relative to $TLV_{drinking\ water}$, $TLV_{open\ water\ bodies}$, $LV_{wastewater}$ were calculated.

The calculation results are shown in Table 3.

Table 3: Coefficient of heavy metal ions concentration in the aqueous extract of galvanic sludge and extraction of acetate-ammonium buffer relative to TLV

element	*aqueous extract*			*extract by an acetate-ammonium buffer*		
	$K_{drinking\ water}$	$K_{open\ water\ bodies}$	$K_{waste\ water}$	$K_{drinking\ water}$	$K_{open\ water\ bodies}$	$K_{waste\ water}$
Al	-	-	-	3.63	18.1	0.242
Ba	-	-	-	0.025	0.024	-

Be	-	-	-	-	-	-
Cd	-	-	-	-	-	-
Co	1.51	15.1	-	9.73	97.3	-
Cr	59.4	148.5	5.94	486	1215	48.6
Cu	11.7	11700	23.4	144	144,000	288
Fe	4.43	26.6	0.443	42.3	254	4.23
Mn	-	-	-	22.2	222	2.22
Mo	416	104000	-	1012	253000	-
Ni	1.54	15.4	0.616	19.3	193	7.72
Pb	-	-	-	-	-	-
Sb	1.58	15.8	-	2.44	24.4	-
Se	1.40	7	-	44.9	224.5	-
Si	16	-	-	41.7	-	-
Sr	-	-	-	0.177	3.10	0.620
Ti	-	-	-	-	-	-
V	-	-	-	-	-	-
Zn	3.47	347	3.47	457	45700	457
B	3.26	3.26	-	11	11	-
Ag	-	-	-	-	-	-
Tl	-	-	-	-	-	-
As	-	-	-	-	-	-

Priority series of elements in a water extract in the decreasing order of magnitude:

$K_{\text{drinking water.}}$ - Mo, Cr, Si, Cu, Fe, Zn, B, Sb, Ni, Co, Se;

$K_{\text{open water bodies}}$ — Mo, Cu, Zn, Cr, Fe, Sb, Ni, Co, Se, B;

$K_{\text{wastewater.}}$ - Cu, Cr, Zn, Ni, Fe.

Priority ranks of elements in an ammonium acetate extract in the decreasing order of magnitude:

$K_{\text{drinking water.}}$ - Mo, Cr, Zn, Cu, Se, Fe, Si, Mn, Ni, B, Co, Al, Sb, Sr, Ba.

$K_{\text{openwater bodies.}}$ - Mo, Cu, Zn, Cr, Fe, Se, Mn, Ni, Co, Sb, Al, B, Sr, Ba.

$K_{\text{waste water.}}$ - Zn, Cu, Cr, Ni, Fe, Mn, Sr, Al.

Water bodies of commercial fishing importance are natural objects into which sewage is discharged.Therefore, the most suitable is a comparison for the series of $K_{\text{openwater bodies}}$ for all indicators (table 3), which is illustrated by the diagram in Fig. 2, provided for convenience in the magnitude of $K_{\text{open water bodies}}$ on a logarithmic scale at base 10.

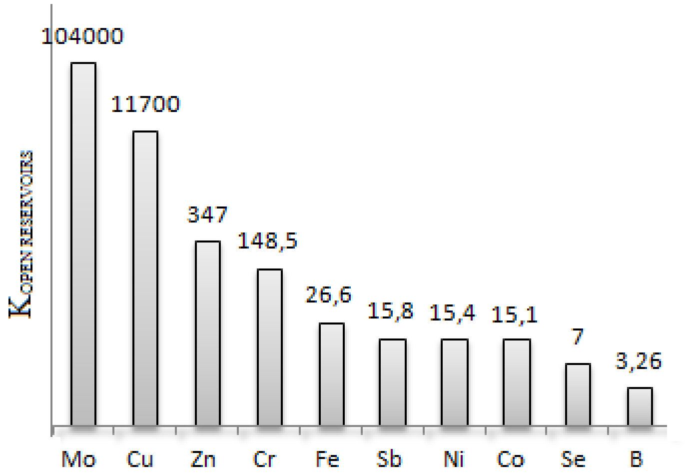

Figure 2: Coefficient of concentration of pollutants of aqueous extract of galvanic sludge relative to TLV in water bodies with a base 10 logarithmic scale.

A significantly larger amount of heavy metals is washed out with ammonium acetate buffer, which reflects the content of the mobile form in the galvanic sludge. Of 23 elements studied, 97.3% in the aqueous extract and 95.8% in the ammonium acetate extract account for five elements Cu, Mo, Si, Zn.

A series of elements by mass content in an aqueous extract:

Si, Mo, Cu, Zn, Cr, B, Fe, Ni, Co, Sb, Se.

A series of elements by mass content in the acetate-ammonium extract:

Zn, Si, Mo, Cu, Cr, Fe, B, Mn, Ni, Sr, Co, Al, Se, Sb, Ba.

Table 4 shows the data on the content in the slurry of elements in a mobile form according to the analysis of aqueous and ammonium acetate extracts from the sludge. Since Clarkes of chemical elements are often used to assess the environmental hazard of pollution of landscape components [10], the table shows data on Clarkes (K) for half-millionaire cities [11], which include the city of Naberezhnye Chelny, where the slurries studied in this work are produced. The soil pollution level regulation is established by regional standards “Background content of heavy metals in the soils of the Republic of Tatarstan” [12], according to which for mobile forms of Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn and B in soils of medium loam, heavy loam and clay indicate the values of C background. For these elements, a relationship is established with a correlation coefficient r = 0.99 between K and $C_{\text{background}}$:

$$K = 15 \cdot C_{\text{background}} + 29, \quad (1)$$

Equation 1 estimates the $C_{\text{background}}$ for Ba, Be, Mo, Sb, Sr, Ti, V, Ag, Tl, As. For Al, Fe, Si, the Clarkes of the corresponding elements were taken as background values (Table 4).Thus, the column $C_{\text{background}}$ of table 4 was completely filled with the corresponding values.

The concentration coefficients for the chemical elements were calculated by the formulas:

$$K_{\text{a. e.}/\text{background}} = \frac{C_{\text{a. e.}}}{C_{\text{background}}}, \ (2)$$

$$K_{\text{e. b. a.-a. b.}/\text{background}} = \frac{C_{\text{e. b. a.-a. b}}}{C_{\text{background}}}, \ (3)$$

The content of a number of metals in the extracts is less than the lower detection limit, which is reflected in table 4 in the concentration coefficients values, as less than some minimum values.

Priority Ratio Series $K_{\text{a. e.}/\text{background}}$ is presented in Fig. 3. Of those 23 elements, 16 heavy metals with $K_{\text{a. e.}/\text{background}} < 1$ (below the line $K_{\text{a. e.}/\text{background}} = 1$ in the diagram) do not pollute the soil when placing sludge in the soil, provided that they are washed out with water.Seven elements are polluting heavy metals $K_{\text{a. e.}/\text{background}} > 1$ (above the line $K_{\text{a. e.}/\text{background}} = 1$ in the diagram), of which five elements Mo, Cu, Cr, Zn and Co are considered as priority ones, which account for more than 99% of $\Sigma(K_{\text{a. e.}/\text{background}})$, i.e. pollution by all heavy metals (Fig. 3).

Table 4: The content of mobile elements in the sludge passing into aqueous extract, passing into extract by acetate-ammonium buffer; Clarke value of an element in the soil of the city with the population of 0.5 million people; regional standards of background content of heavy metals in soils of RT; coefficients of concentration are based on the content of the elements passing into aqueous extract relative to $C_{\text{background}}$, in terms of the content of the elements passing into extract by acetate-ammonium buffer relative to $C_{\text{background}}$

element	*Concentration in the aqueous extract, mg / kg*	*Concentration in the extract by acetate-ammonium buffer, mg / kg*	*Clarke, mg / kg*	$C_{\text{background}}$, *mg / kg*	$K_{ae / background}$	$K_{eba\text{-}ab / background}$
Al	<0.0001	7.25	37360	37360 [11]	<0.000000003	0.0002
Ba	<0.00003	0.18	1091.4	73 *	<0.0000004	0.0025
Be	<0.00001	<0.00001	2.8	0.19 *	<0.000054	<0.000054
Cd	<0.00005	<0.00005	0.8	0.1 [12]	<0.0005	<0.0005

Co	0.75	9.73	14.4	0.1 [12]	7.5	97
Cr	14.9	243	55	0.3 [12]	49.7	810
Cu	58.7	1444	30.1	0.2 [12]	293.5	7220
Fe	6.64	127	20110	20110 [11]	0.0003	0.0063
Mn	<0.00003	22.2	715.2	45 [12]	<0.0000007	0.493
Mo	524	2527	2.2	0.15 *	3573	17230
Ni	0.77	19.3	28	1 [12]	0.77	nineteen
Pb	<0.0008	<0.0008	45.6	1 [12]	<0.0008	<0.0008
Sb	0.4	1.22	1	0.067 *	6	18.3
Se	0.07	4.49	0.24	0.4 [11]	0.18	11.2
Si	799	4165	261200	261200 [11]	0.003	0.016
Sr	<0.00001	12.4	359.2	23.9 *	<0.0000004	0.52
Ti	<0.0001	<0.0001	4378.2	292 *	<0.00000034	<0.00000034
V	<0.0002	<0.0002	78.9	5.3 *	<0.000038	<0.000038
Zn	17.4	4570	115.8	1 [12]	17.4	4570
B	8.13	55	45	3 [12]	2.7	18.3
Ag	<0.0003	<0.0003	0.4	0.027 *	<0.0113	<0.0113
Tl	<0.0015	<0.0015	1	0.067 *	<0.0225	<0.0225
As	<0.001	<0.001	10	0.67 *	<0.0015	<0.0015

Note: * - calculated by equation 1.

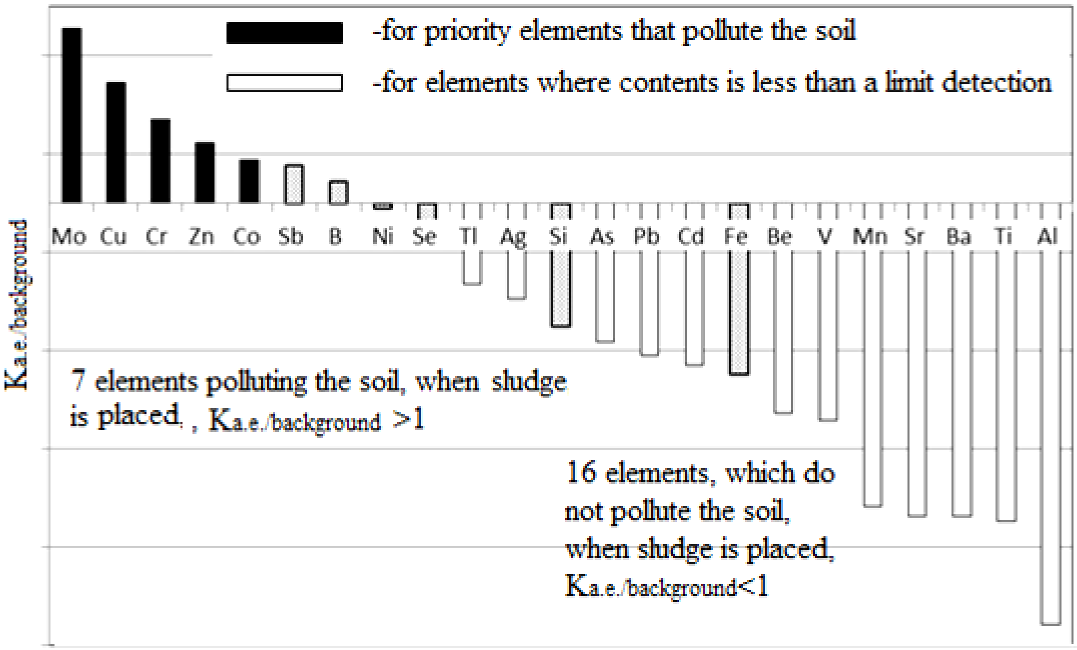

Figure 3:A priority series of elements according to the coefficient of concentration Kae / background when washing sludge water.

An elements priority series when washing out with water from the sludge in the order of decreasing the concentration coefficient: Mo, Cu, Cr, Zn, Co, Sb, B, Ni, Se, (Tl), (Ag), Si, (As), (Pb), (Cd), Fe, (Be), (V), (Mn), (Sr), (Ba), (Ti), (Al). Elements in brackets which content in the water extract is less than the detection limit are indicated.

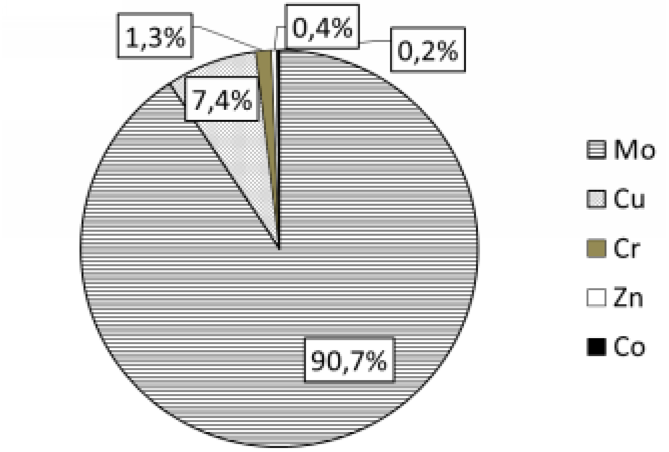

Figure 4: A contribution of priority elements to soil pollution by the sludge through an aqueous extract.

In natural soil conditions, the leaching medium may act on the sludge not in the form of “pure water”, but in the form of some more effective buffer medium, which is well mimicked by ammonium acetate buffer.

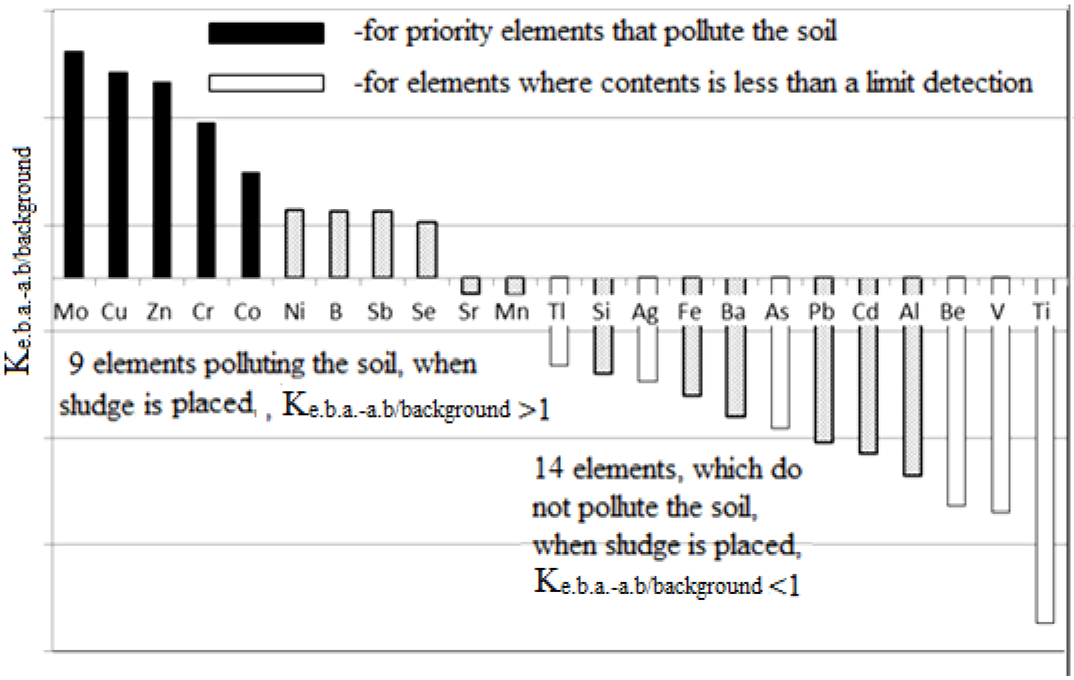

Figure 5: A series of priority elements according to concentration coefficient K eba-ab / background when washing the sludge with ammonium acetate buffer.

In this case, the priority of heavy metals is illustrated by the diagram in Fig. 6. The amount of polluting the soil here is nine elements, five of which are priority: Mo, Cu, Zn, Cr and Co. They account for more than 99% of Σ ($K_{\text{eba-ab / background}}$), that is, pollution by all heavy metals when they are washed out with a buffer (Fig. 6).

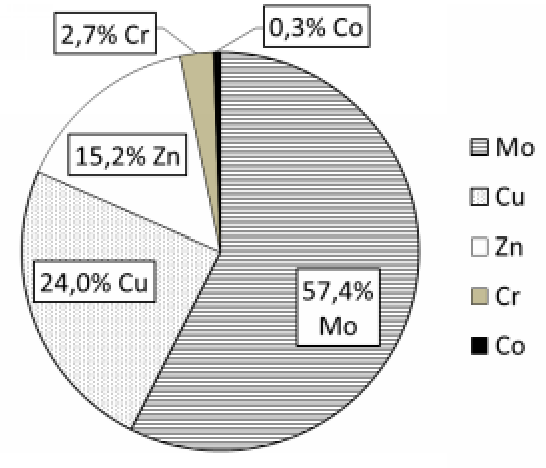

Figure 6: A contribution of priority elements to pollution of the soiled sludge through an ammonium acetate extract.

A series of priority elements when washing with ammonium acetate buffer from sludge in the order of decreasing concentration coefficient is: Mo, Cu, Zn, Cr, Co, Ni, B, Sb, Se, Sr, Mn, (Tl), Si, (Ag), Fe, Ba, (As), Pb, Cd, Al, (Be), (V), (Ti). The last two series have insignificant differences, although emission through an ammonium acetate buffer predominates in almost all elements with the content greater than the opening minimum.

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IV. SUMMARY

The galvanic production sludge contains elements polluting the water phase, which provide a high hazard to the environment and pollute water bodies and soil. Most indicators of the galvanic sludge water extract exceed the water standards of the three main standardized water bodies: drinking, household purposes, water bodies for commercial fishery purposes, and wastewater. Thus, due to the high solubility of most of the galvanic sludge, the pollutants in the form of heavy metal ions are relatively easily washed into the aqueous phase and pollute water bodies and the environment.

The excess of heavy metal ions over the normative indicators for wastewater in an ammonium acetate extract in many cases exceeds 3, that is, it is rough [9].The prior polluting heavy metals in the mobile form are (in the order of decreasing values) Mo, Cu, Zn and Cr, which account for more than 99% of the pollution of the aqueous phase with sludge from galvanic production.

An analysis of the results shows that the neutralization of sludge by heavy metals is possible when elements such as Mo, Cu, Zn, Cr, Co and, probably, Ni, are primarily converted to insoluble forms or removed from the sludge.

V. CONCLUSIONS

The results obtained to exclude the possibility of storage or any placement of galvanic sludge and necessitate its disposal and processing. Galvanic sludge should not be stored, but processed, which should be aimed at extracting or turning into an insoluble form, primarily, priority heavy metals, in this case, Mo, Cu, Zn, Cr, Co and Ni.

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